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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0008034 A1****Chen et al.**(43) **Pub. Date: Jan. 24, 2002**(54) **APPARATUS AND METHOD FOR
ELECTROCHEMICALLY DEPOSITING
METAL ON A SEMICONDUCTOR
WORKPIECE**(76) **Inventors: Linlin Chen, Plano, TX (US); Gregory
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Seattle, WA 98101-2347 (US)**(21) **Appl. No.: 09/732,513**(22) **Filed: Dec. 7, 2000****Related U.S. Application Data**

(63) Continuation of application No. 09/387,099, filed on Aug. 31, 1999, now Pat. No. 6,277,263, which is a continuation of application No. PCT/US99/06306, filed on Mar. 22, 1999, which is a continuation-in-part of application No. 09/045,245, filed on Mar. 20, 1998, now Pat. No. 6,197,181 and which is a non-provisional of provisional application No. 60/085,675, filed on May 15, 1998. Continuation of application No. PCT/US00/10120, filed on Apr. 13, 2000. Non-provisional of provisional application No. 60/182,

160, filed on Feb. 14, 2000. Non-provisional of provisional application No. 60/143,769, filed on Jul. 12, 1999. Non-provisional of provisional application No. 60/129,055, filed on Apr. 13, 1999. Non-provisional of provisional application No. 60/206,663, filed on May 24, 2000.

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C25D 5/10; C25D 5/50; C25D 3/38**
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205/186; 205/170; 205/115;
204/272; 205/182; 205/133;
205/187; 205/227; 428/615**(57) **ABSTRACT**

A process for metallization of a workpiece, such as a semiconductor workpiece. In an embodiment, an alkaline electrolytic copper bath is used to electroplate copper onto a seed layer, electroplate copper directly onto a barrier layer material, or enhance an ultra-thin copper seed layer which has been deposited on the barrier layer using a deposition process such as PVD. The resulting copper layer provides an excellent conformal copper coating that fills trenches, vias, and other microstructures in the workpiece. When used for seed layer enhancement, the resulting copper seed layer provide an excellent conformal copper coating that allows the microstructures to be filled with a copper layer having good uniformity using electrochemical deposition techniques. Further, copper layers that are electroplated in the disclosed manner exhibit low sheet resistance and are readily annealed at low temperatures.

Fig. 1.

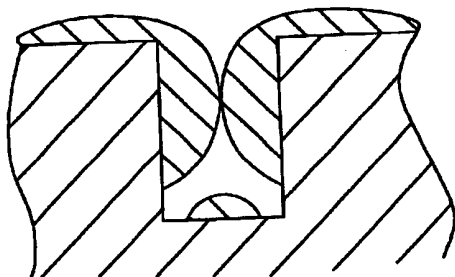


Fig. 2A.

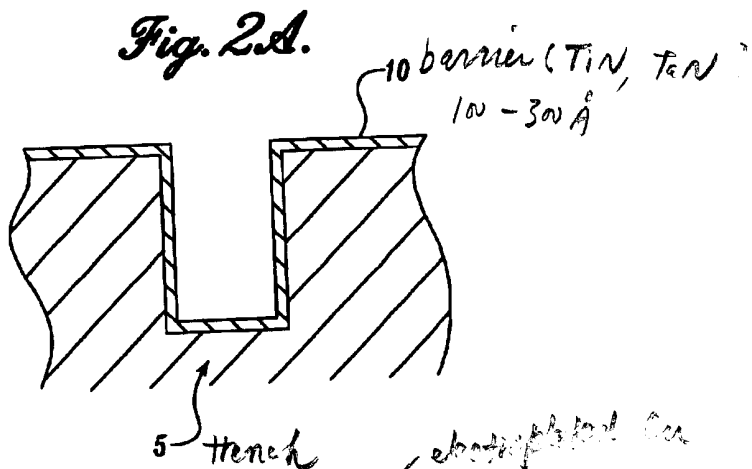


Fig. 2B.

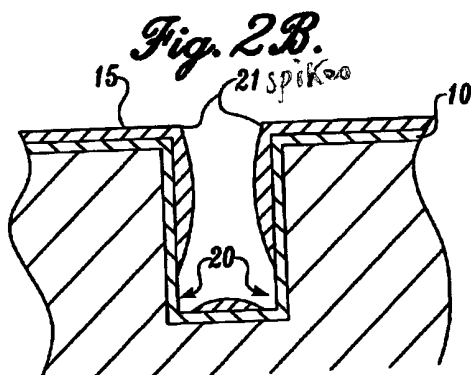


Fig. 2C.

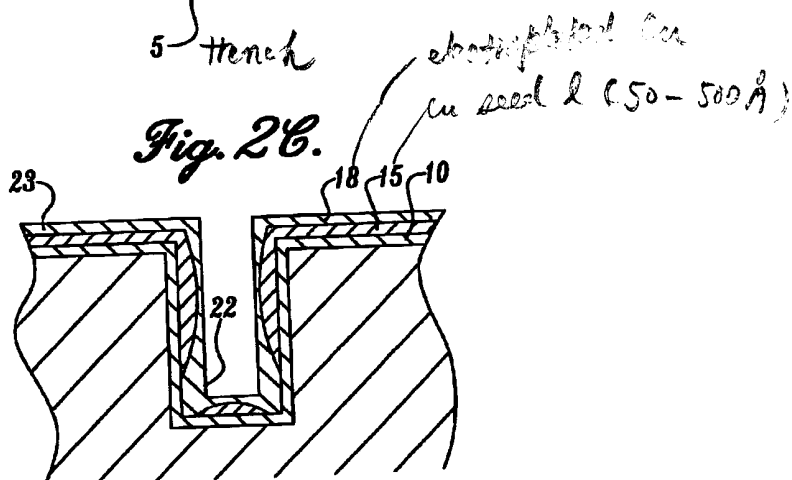


Fig. 2D.

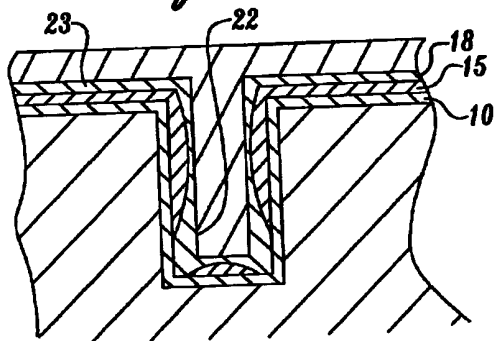
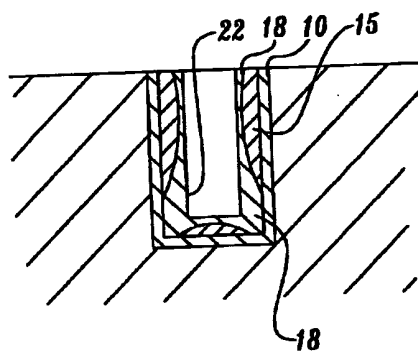


Fig. 2E.



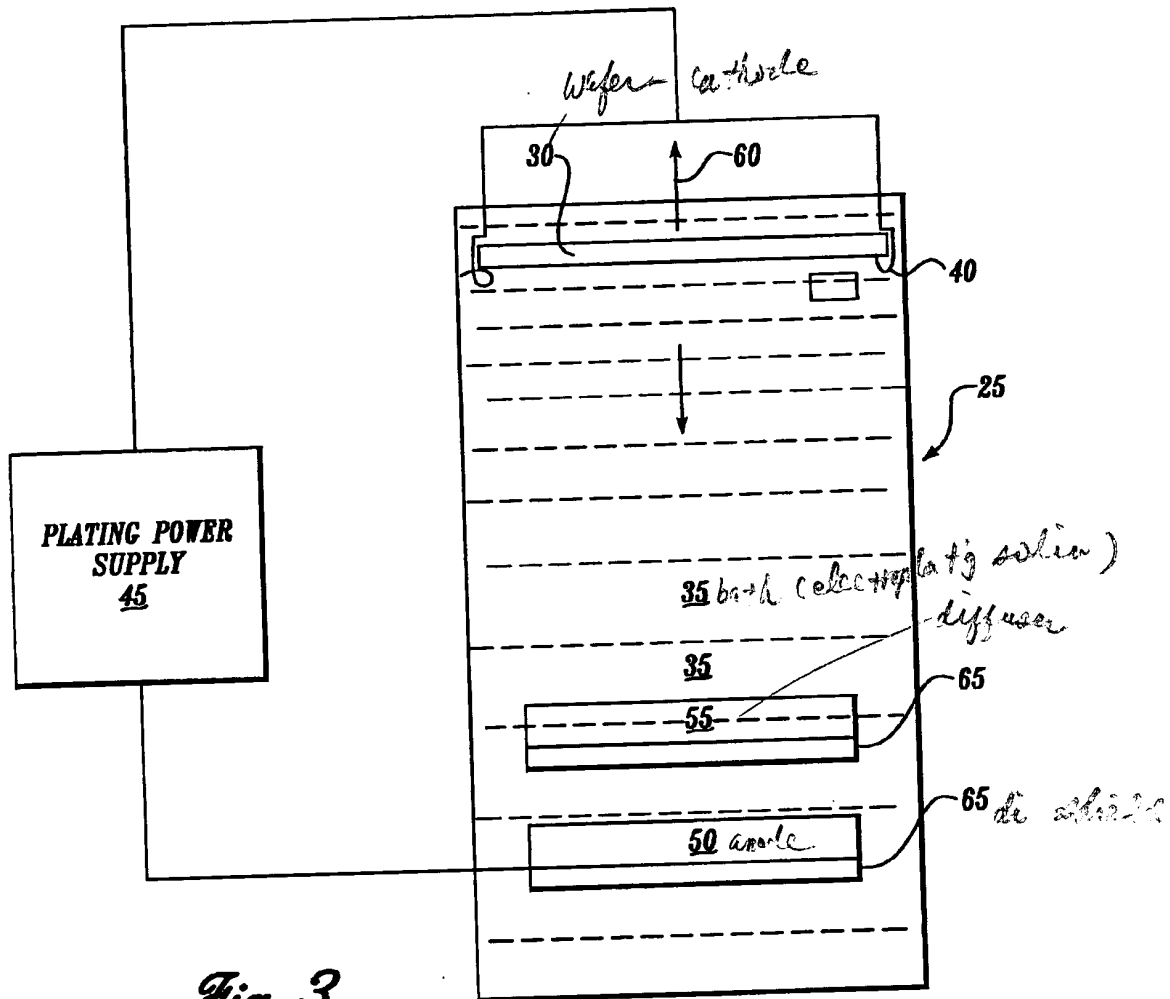
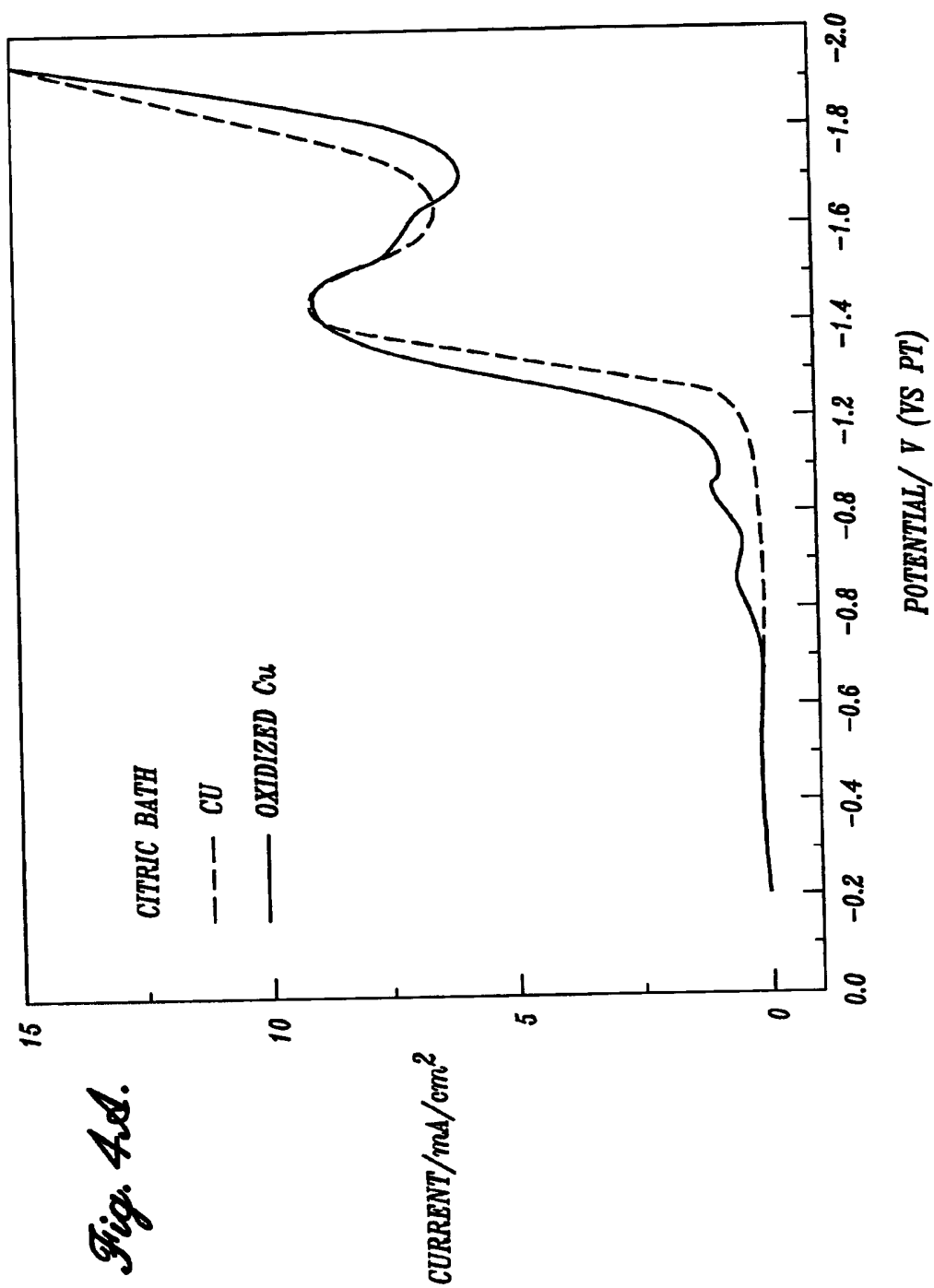
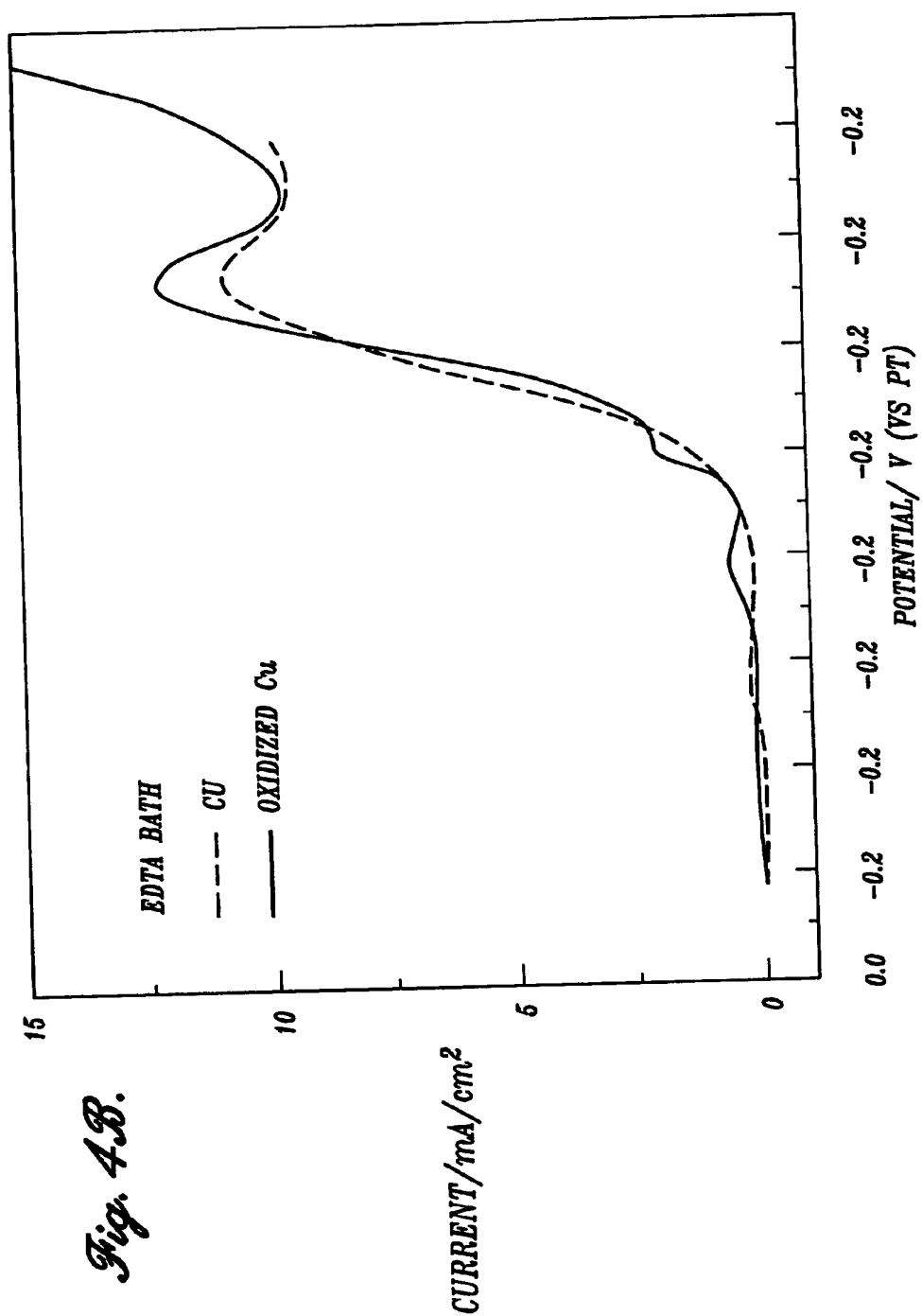
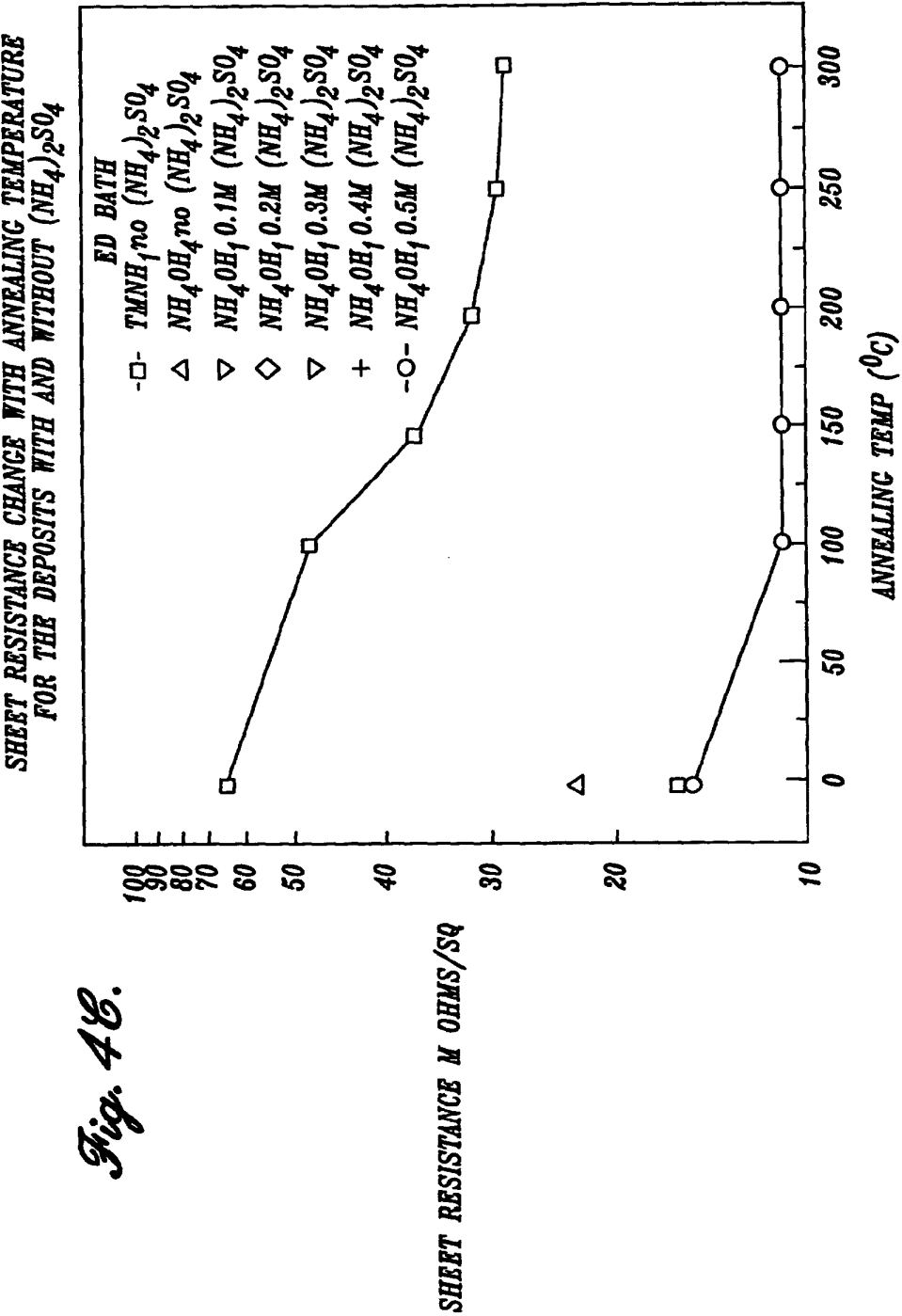
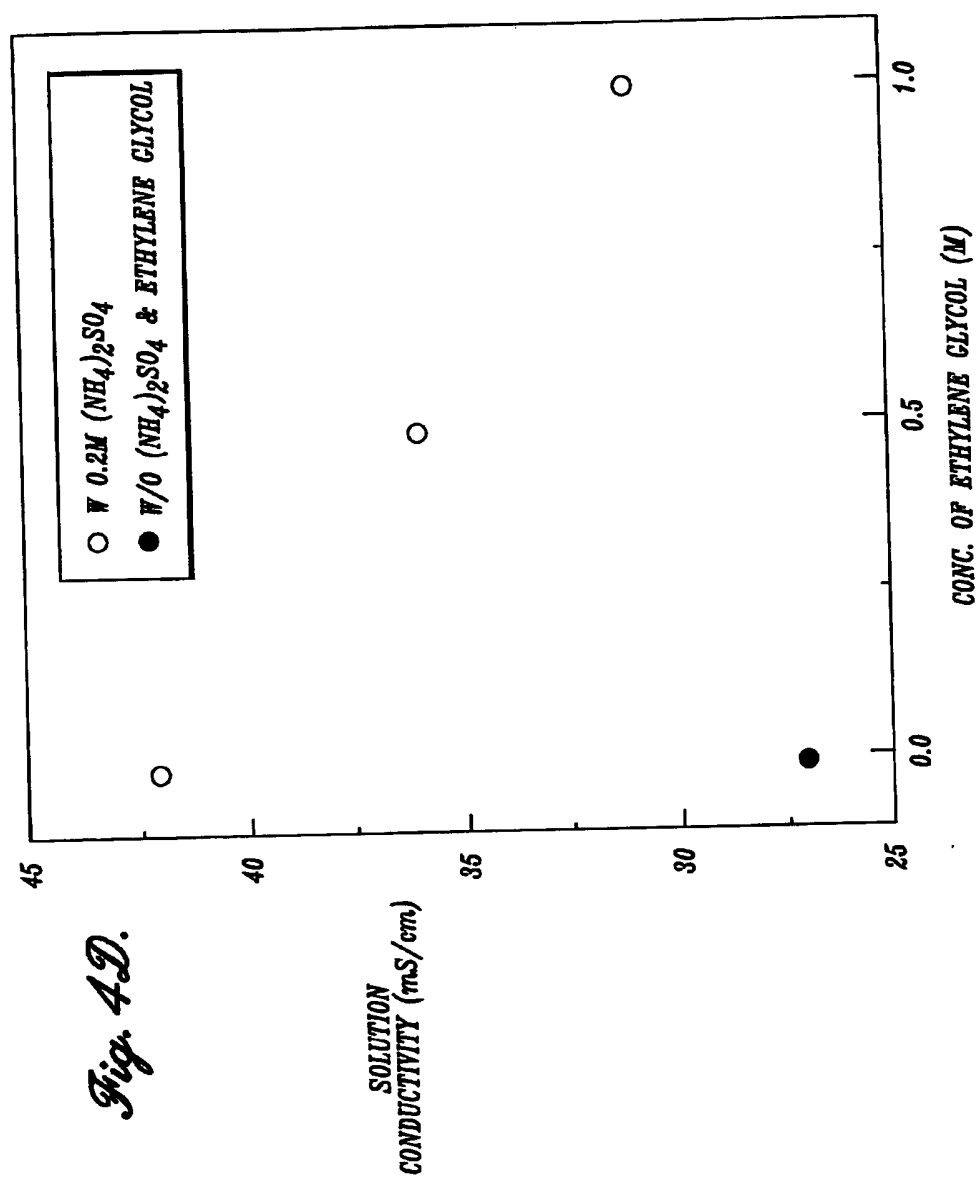


Fig. 3.









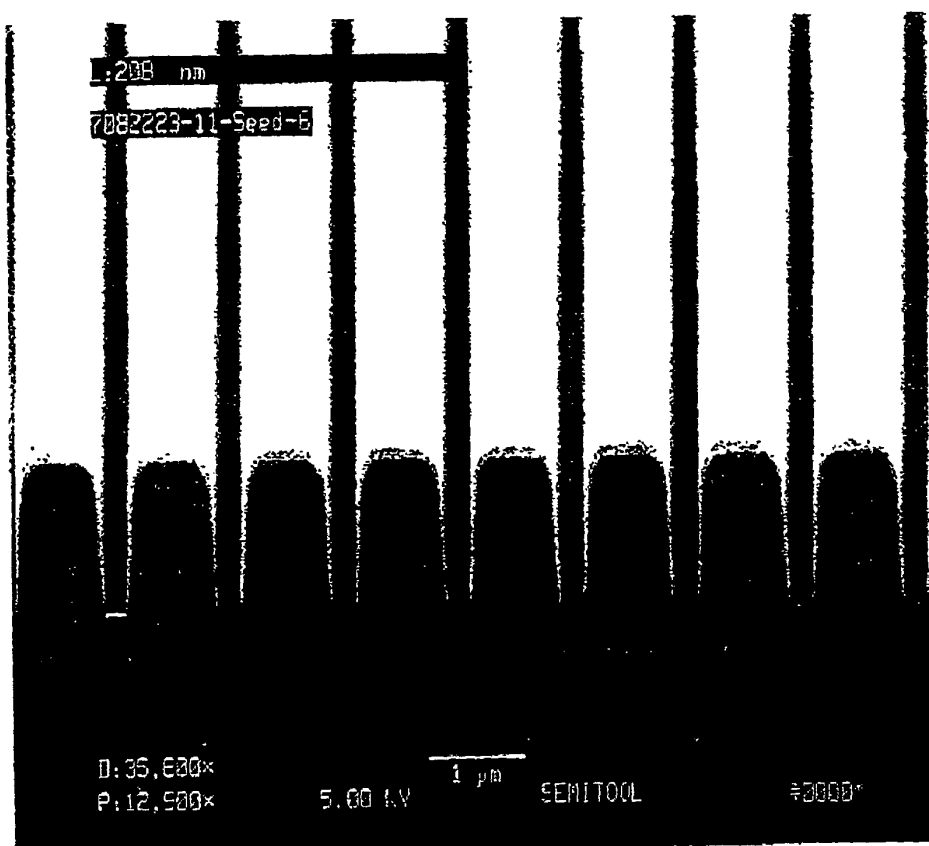


Fig.5.

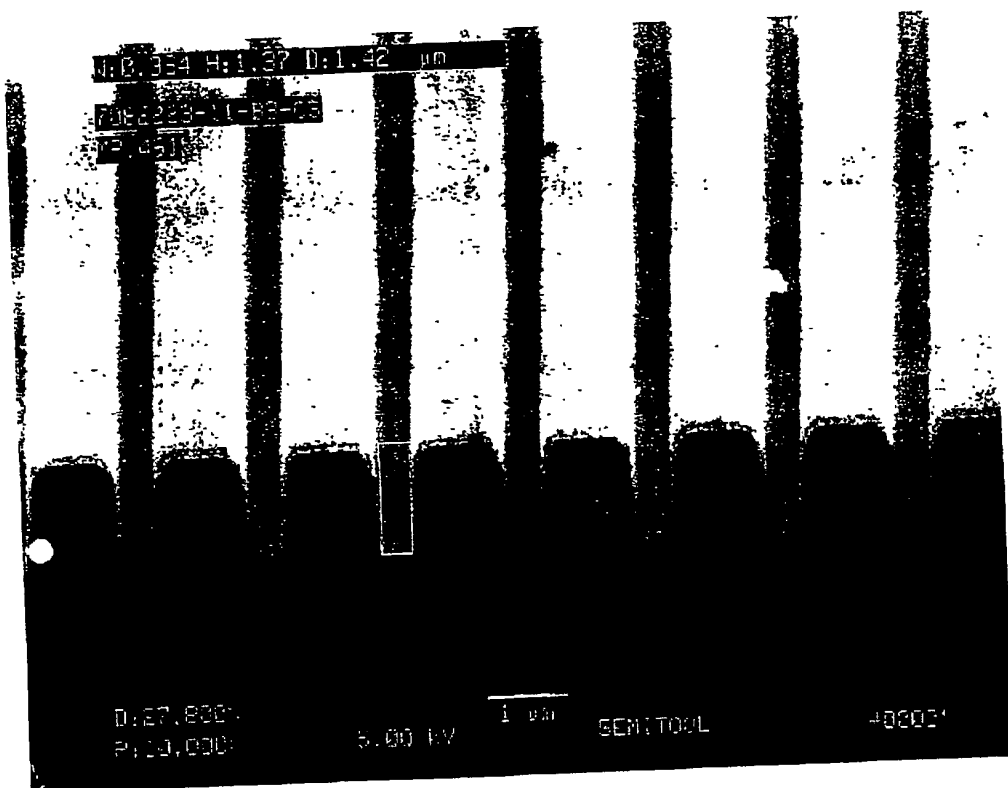


Fig.6A.

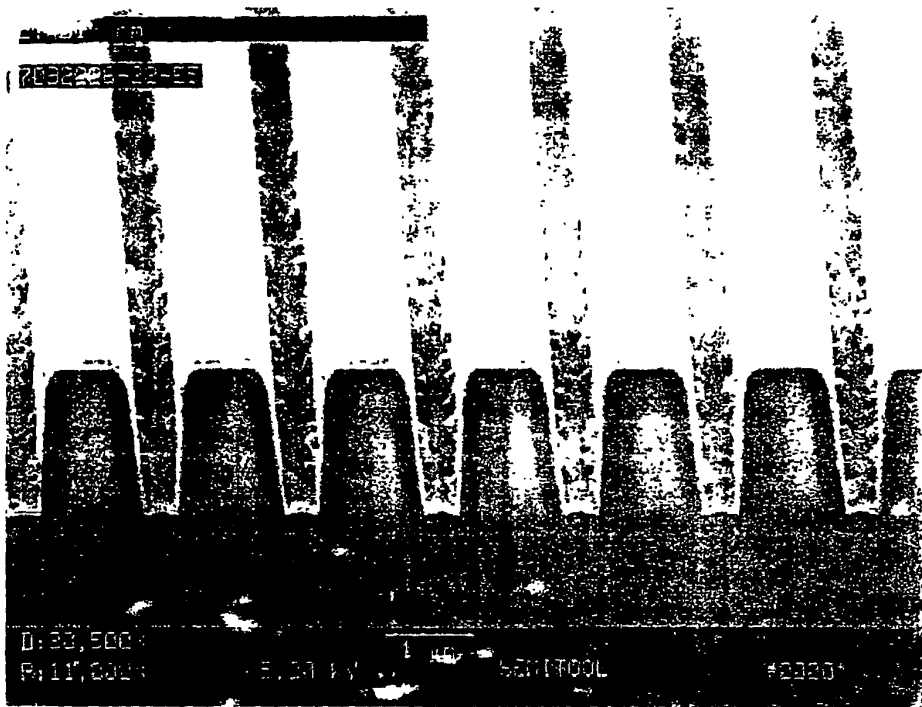


Fig.6B.

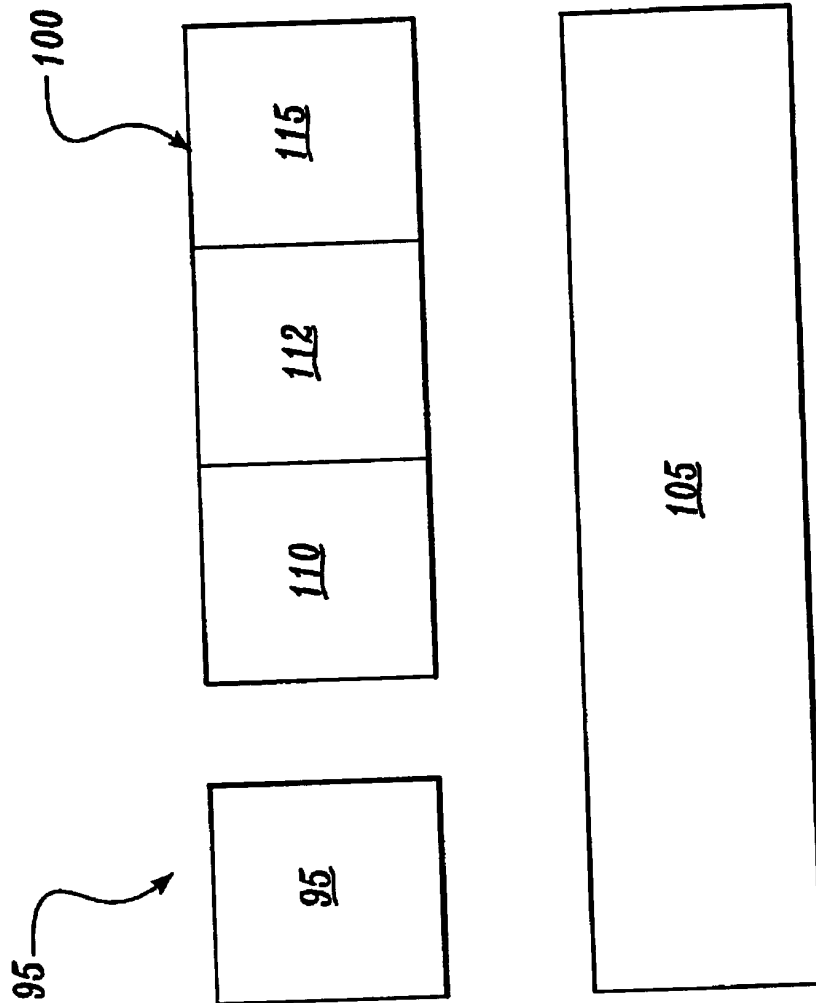
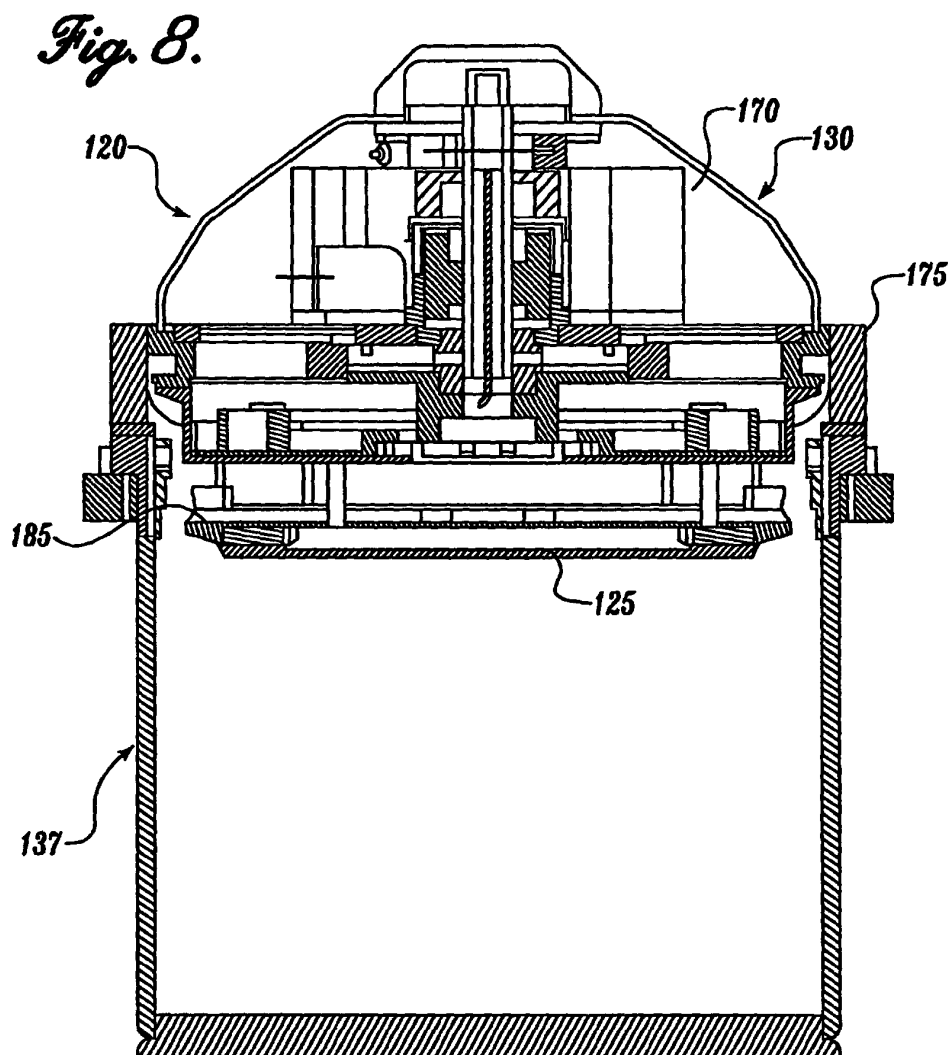


Fig. 7.



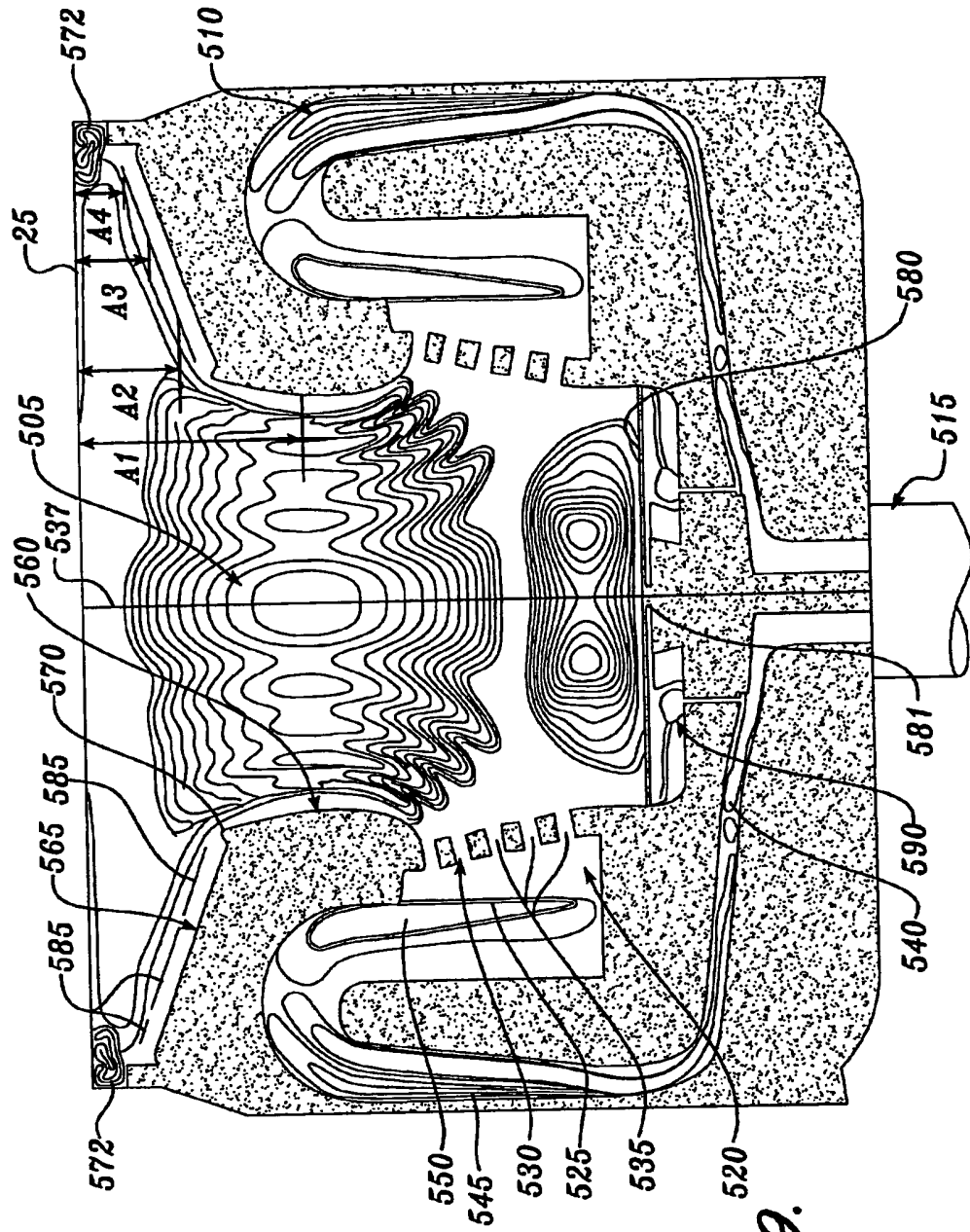


Fig. 9.

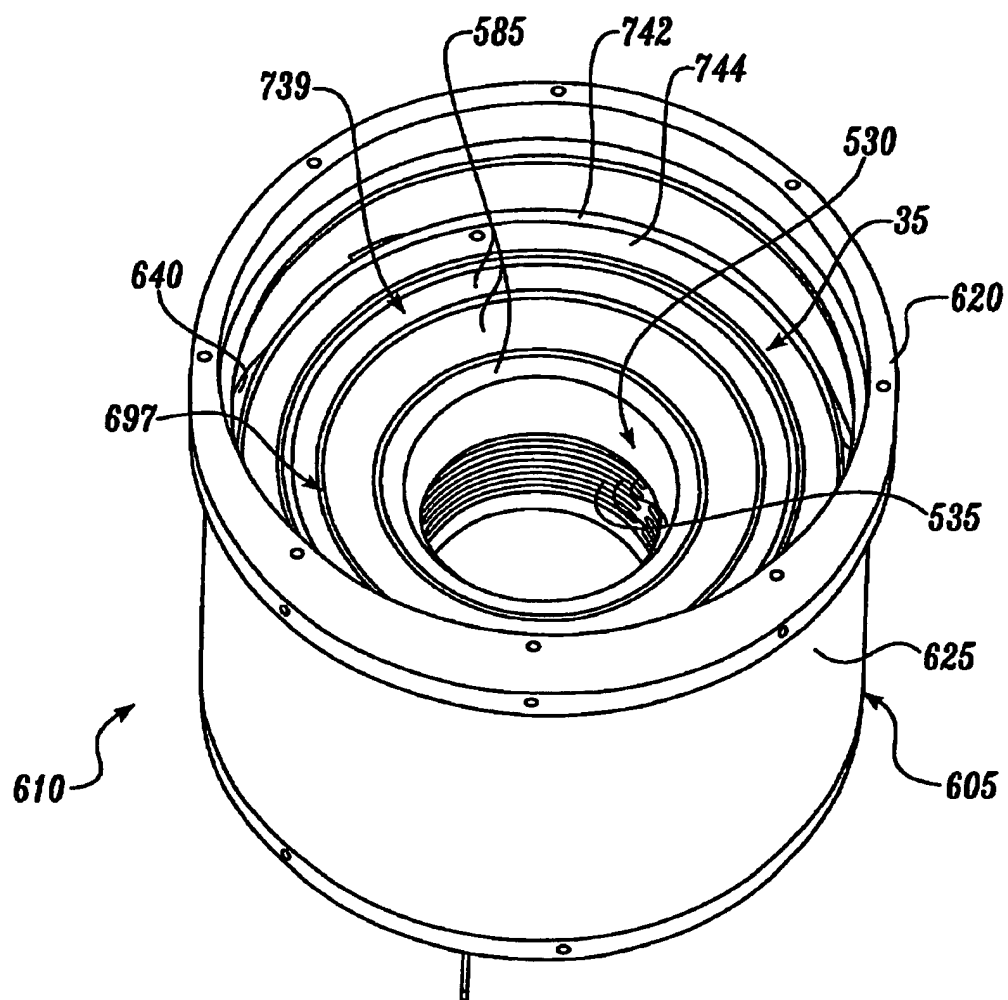


Fig. 10A.

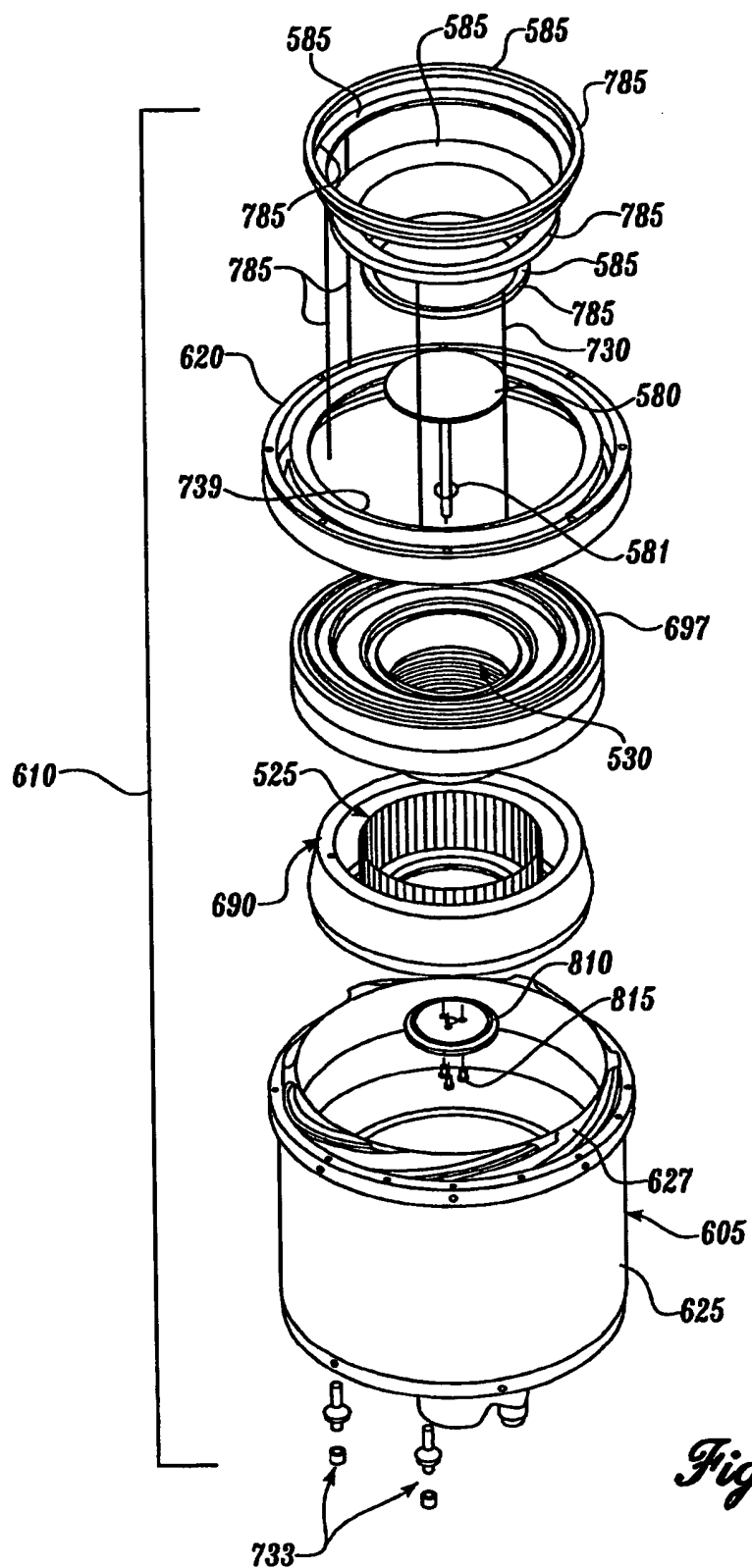


Fig. 10B.

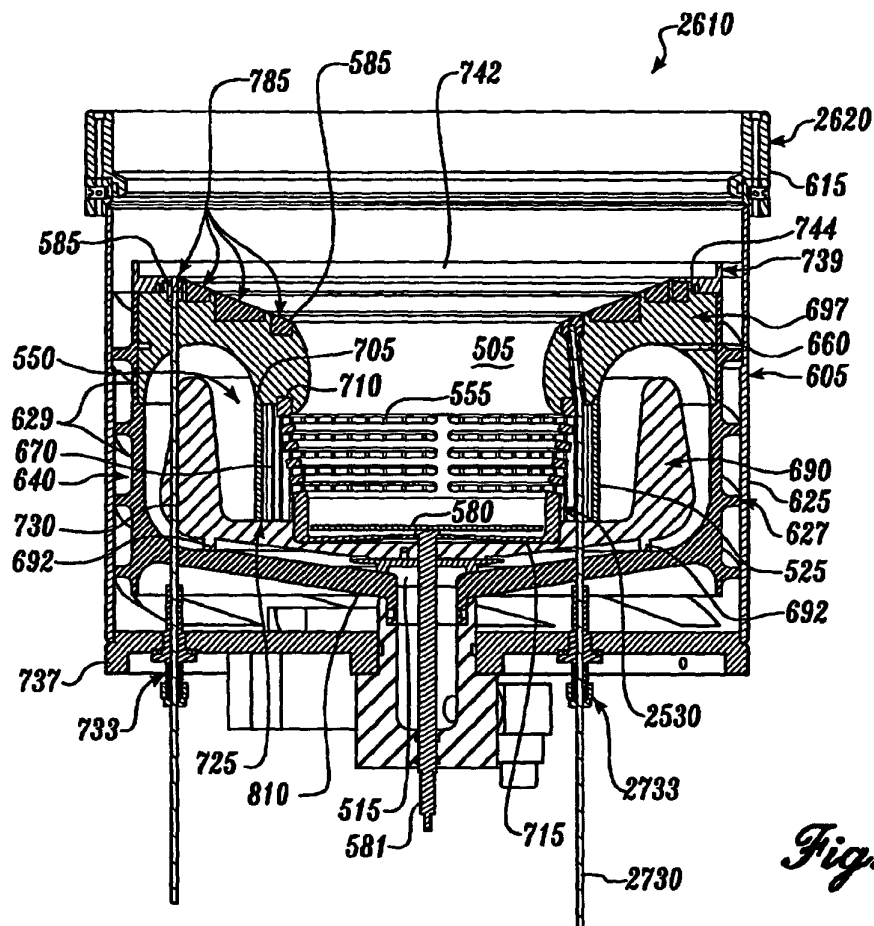


Fig. 11.

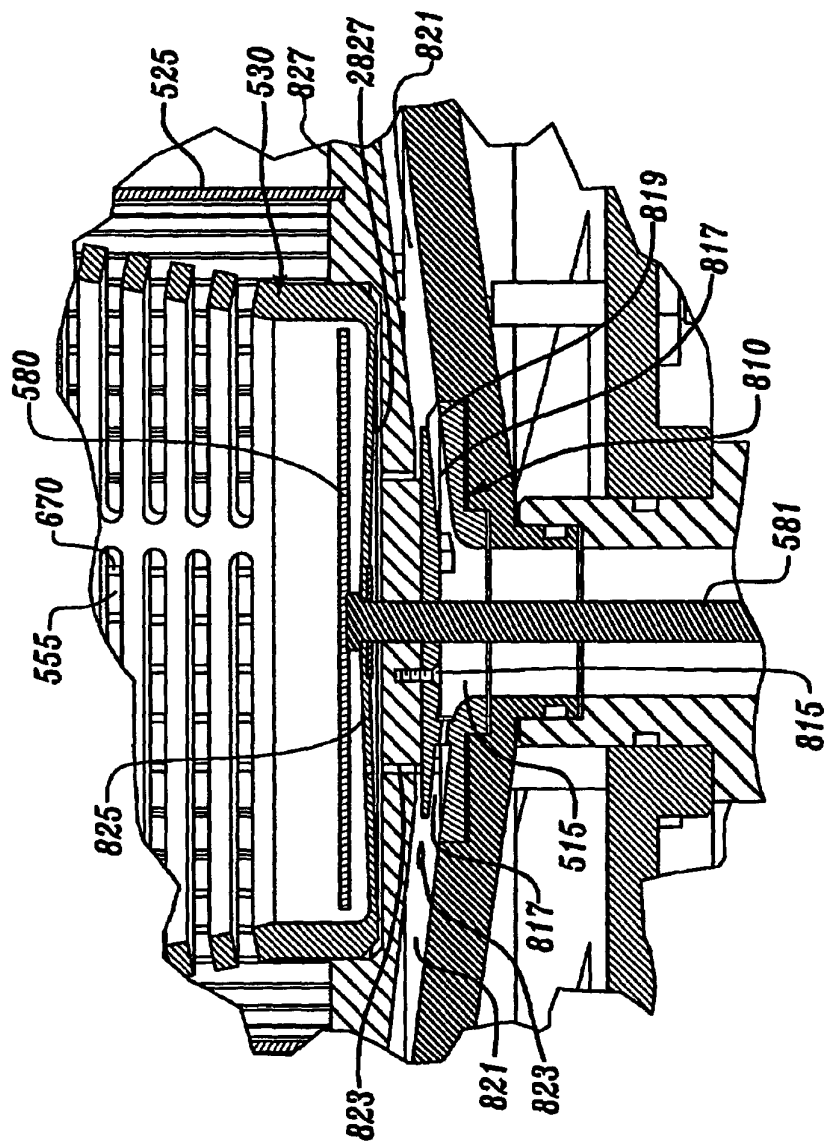


Fig. 12.

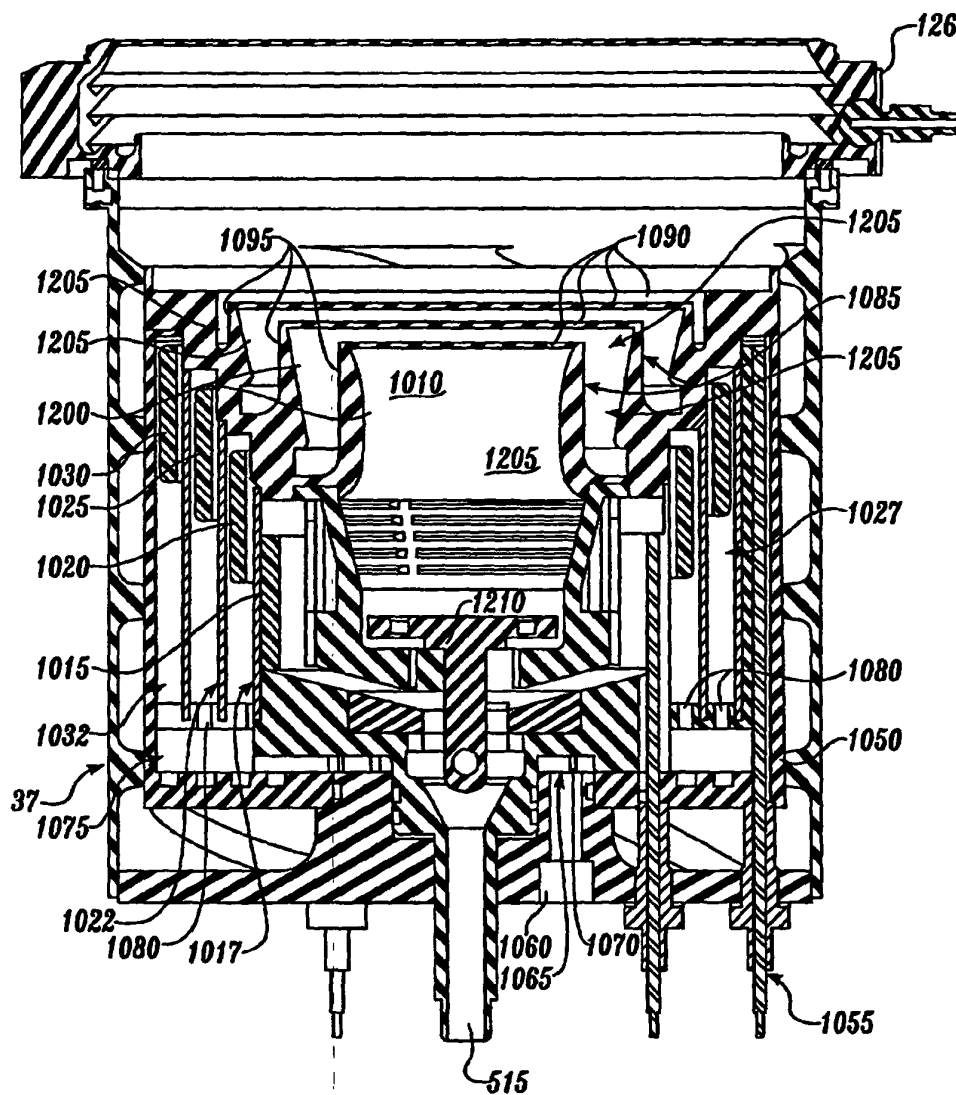


Fig. 13.

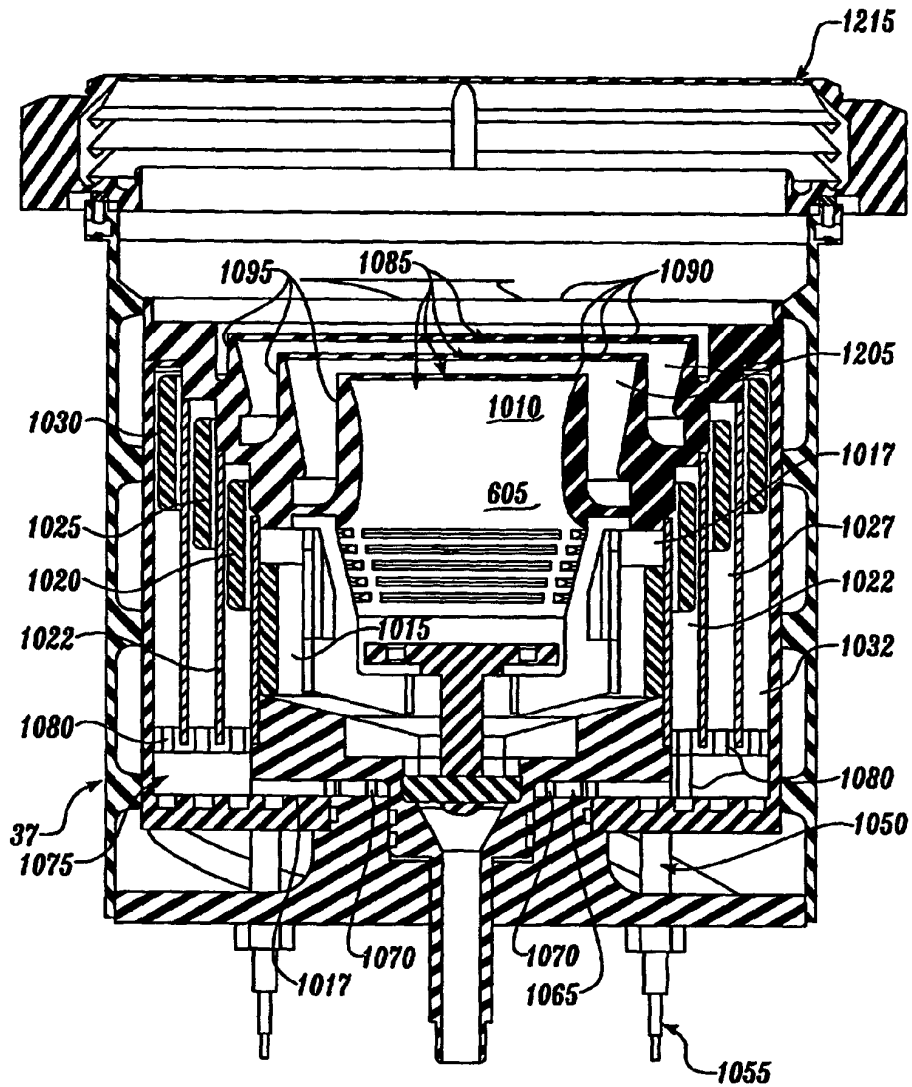


Fig. 14.

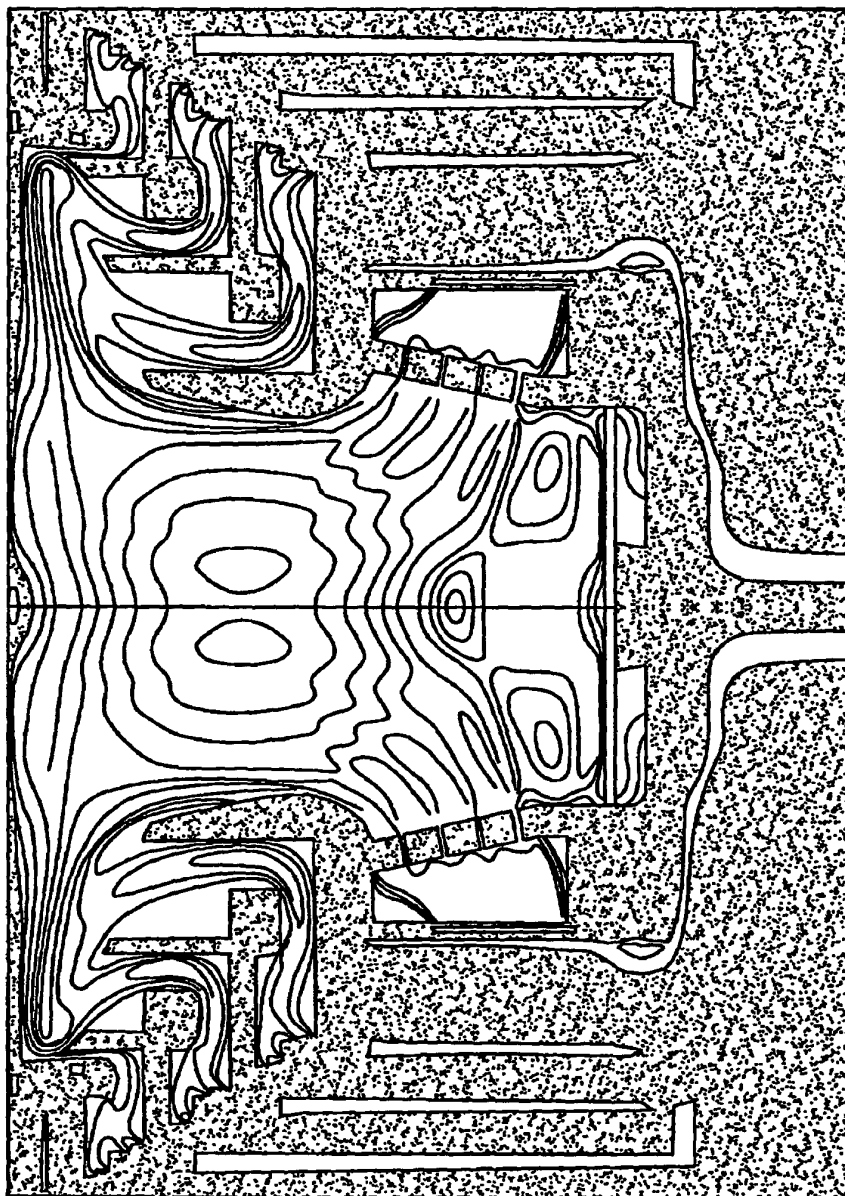


Fig. 15.

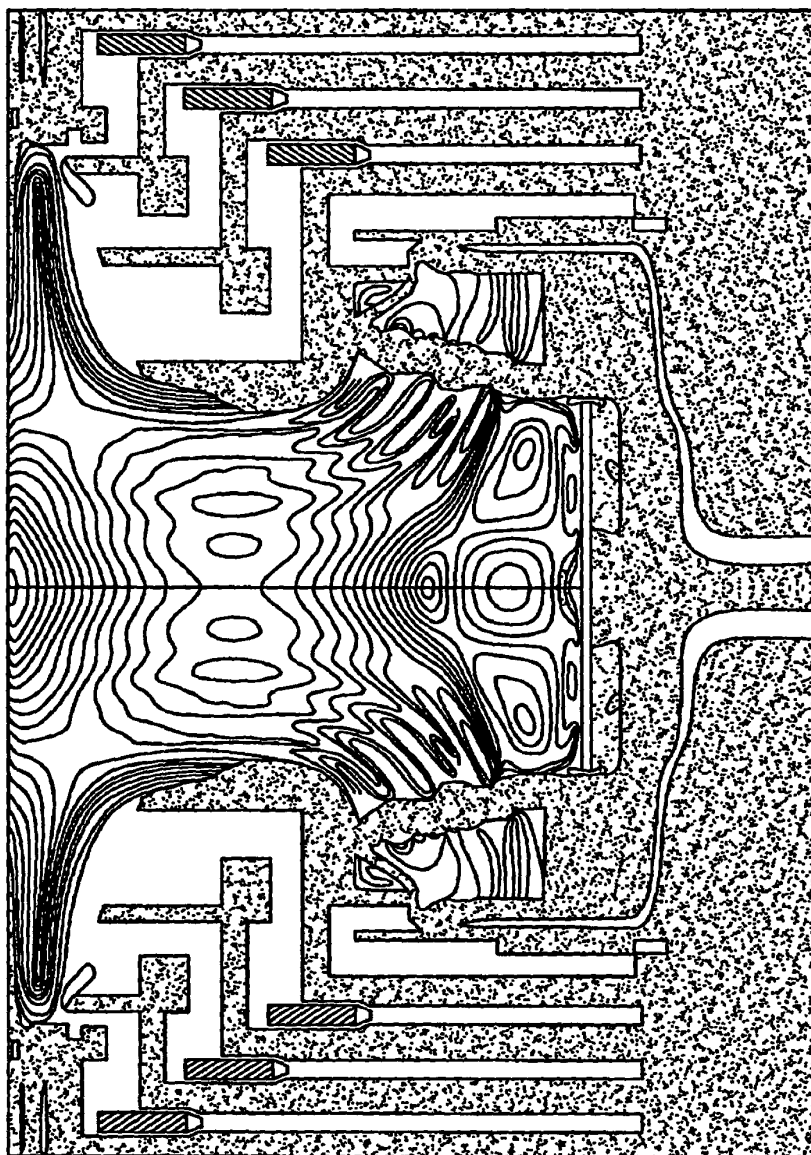


Fig. 16.

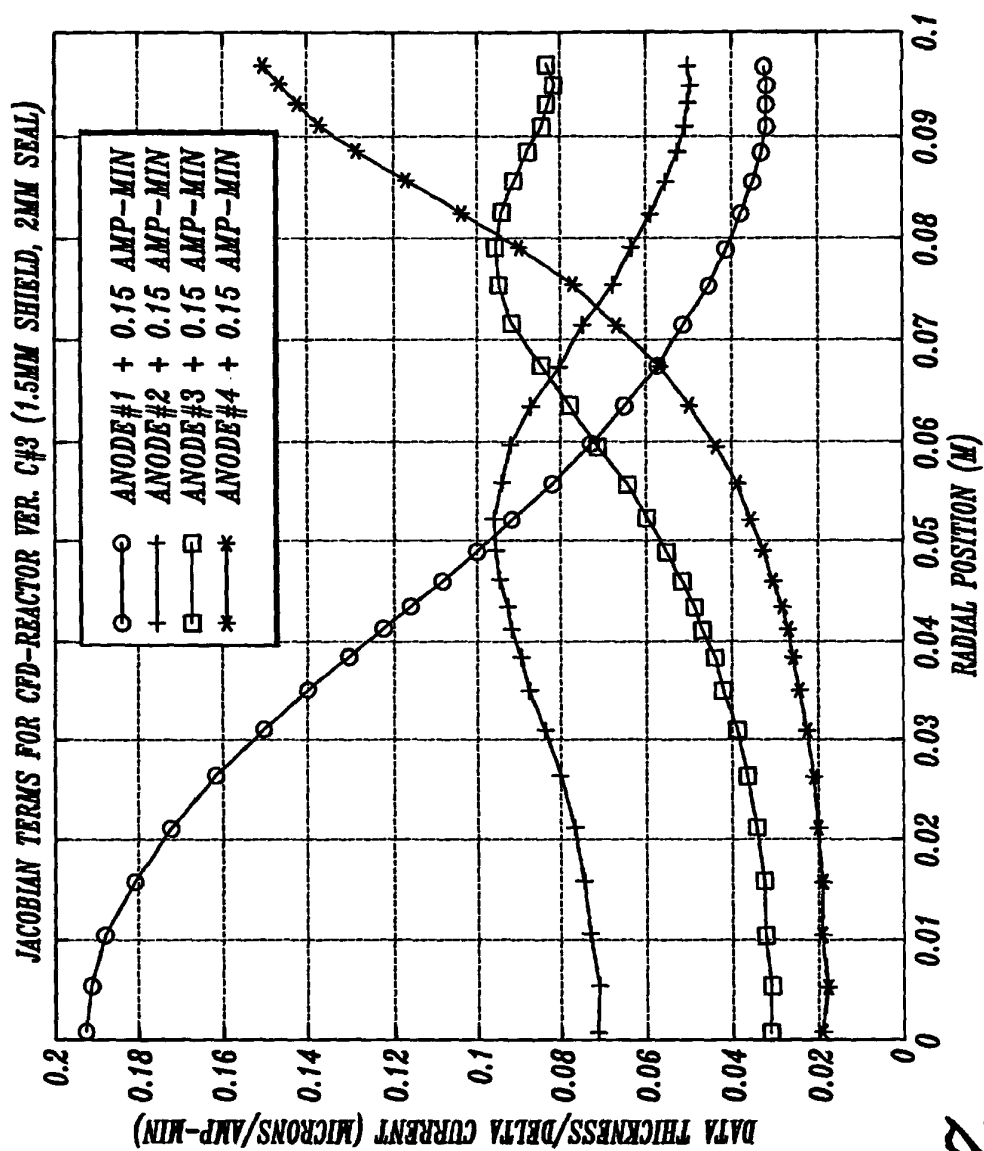


Fig. 17.

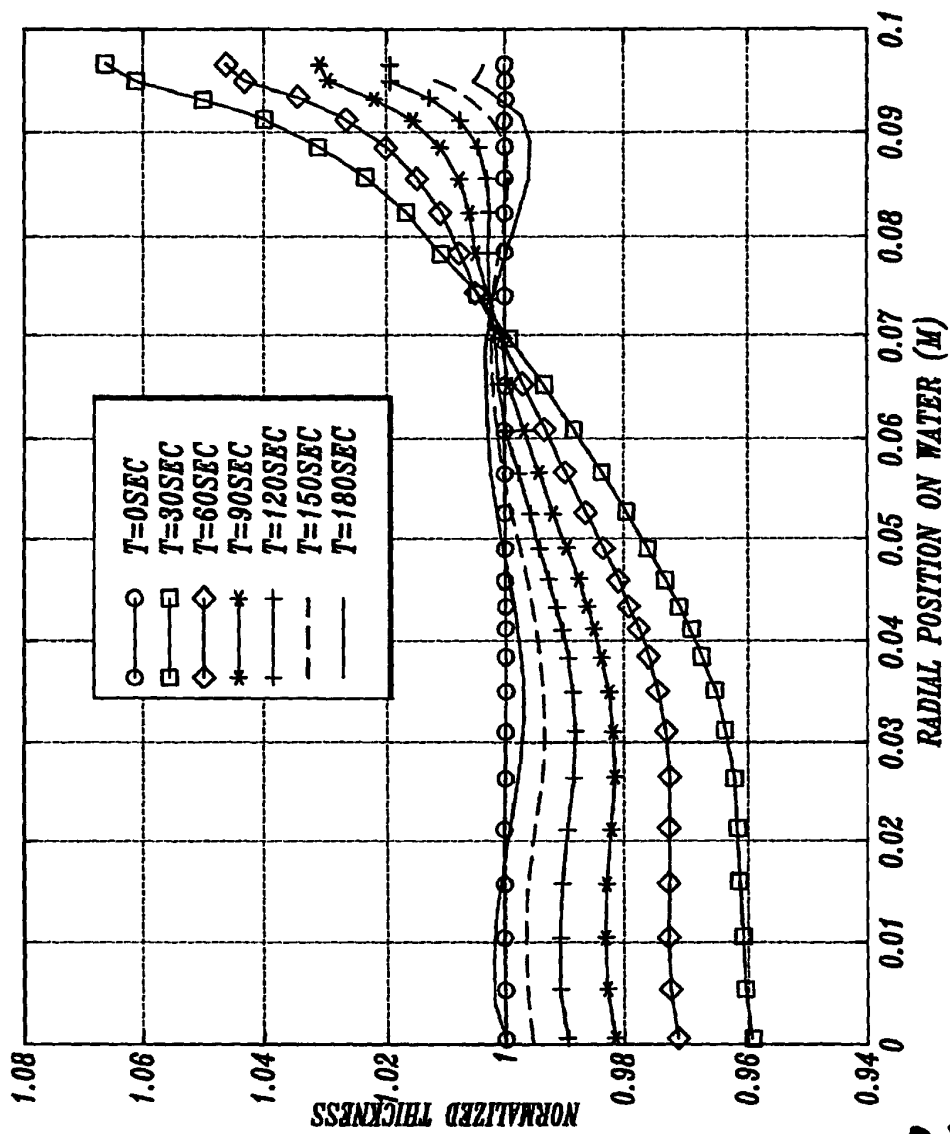


Fig. 18.

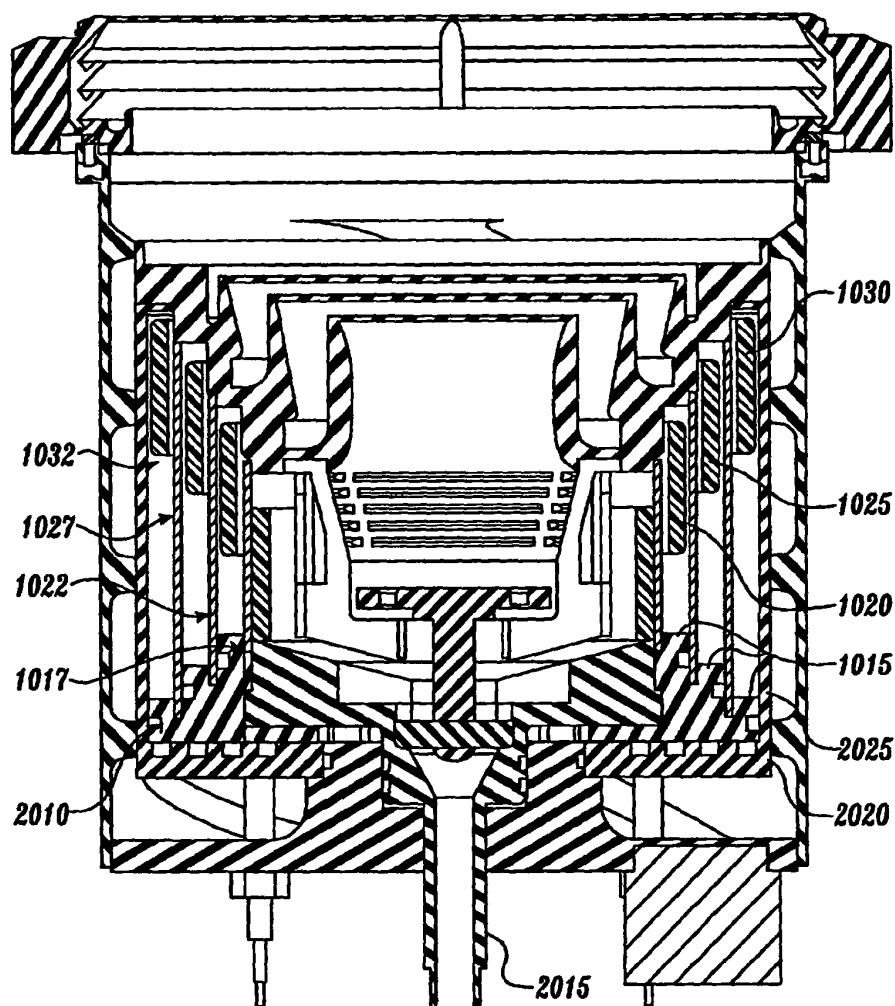


Fig. 19.

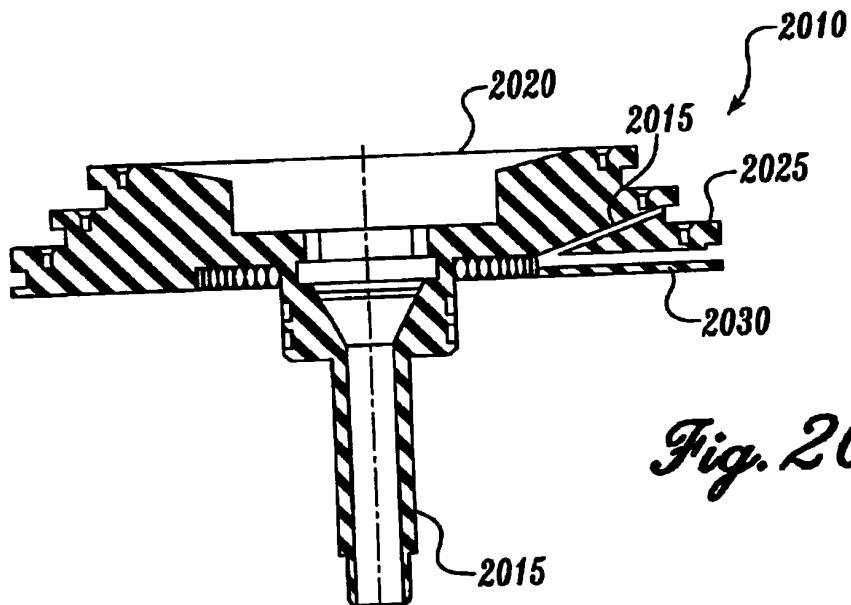


Fig. 20.

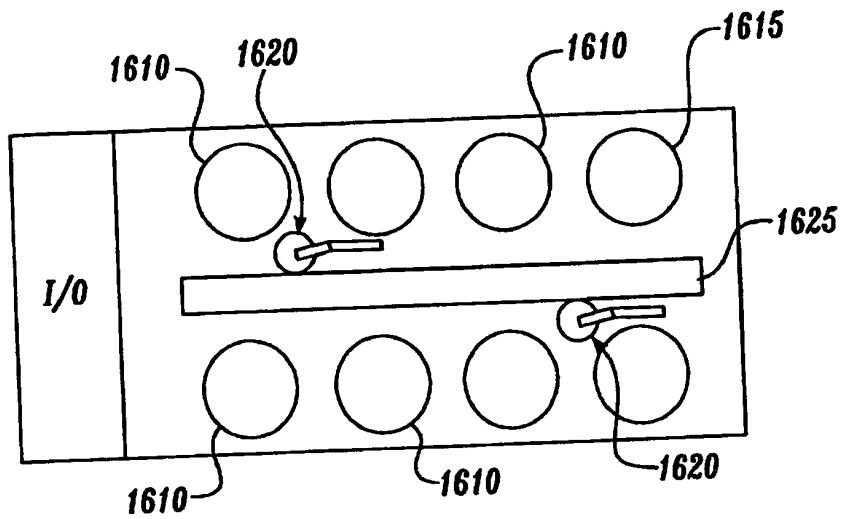


Fig. 21.

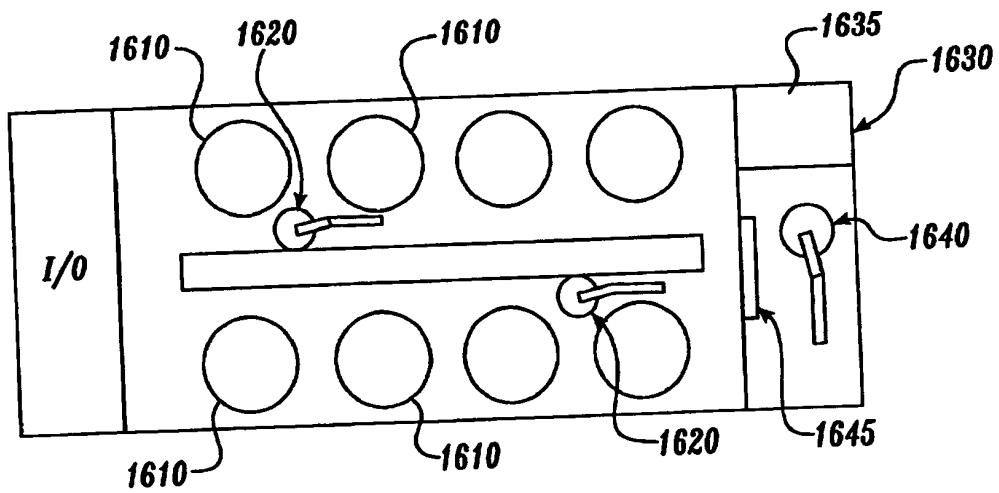


Fig. 22.

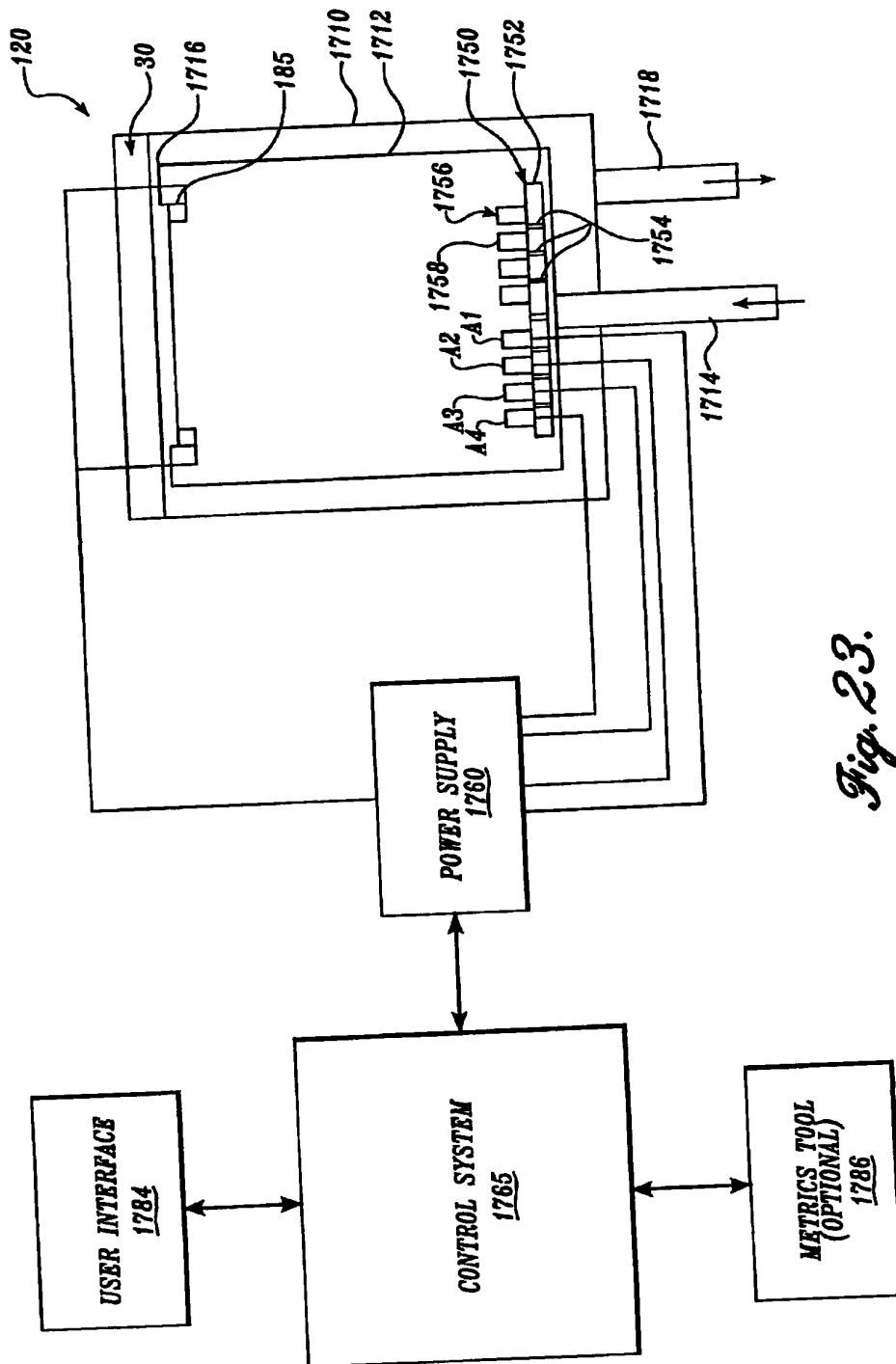


Fig. 23.

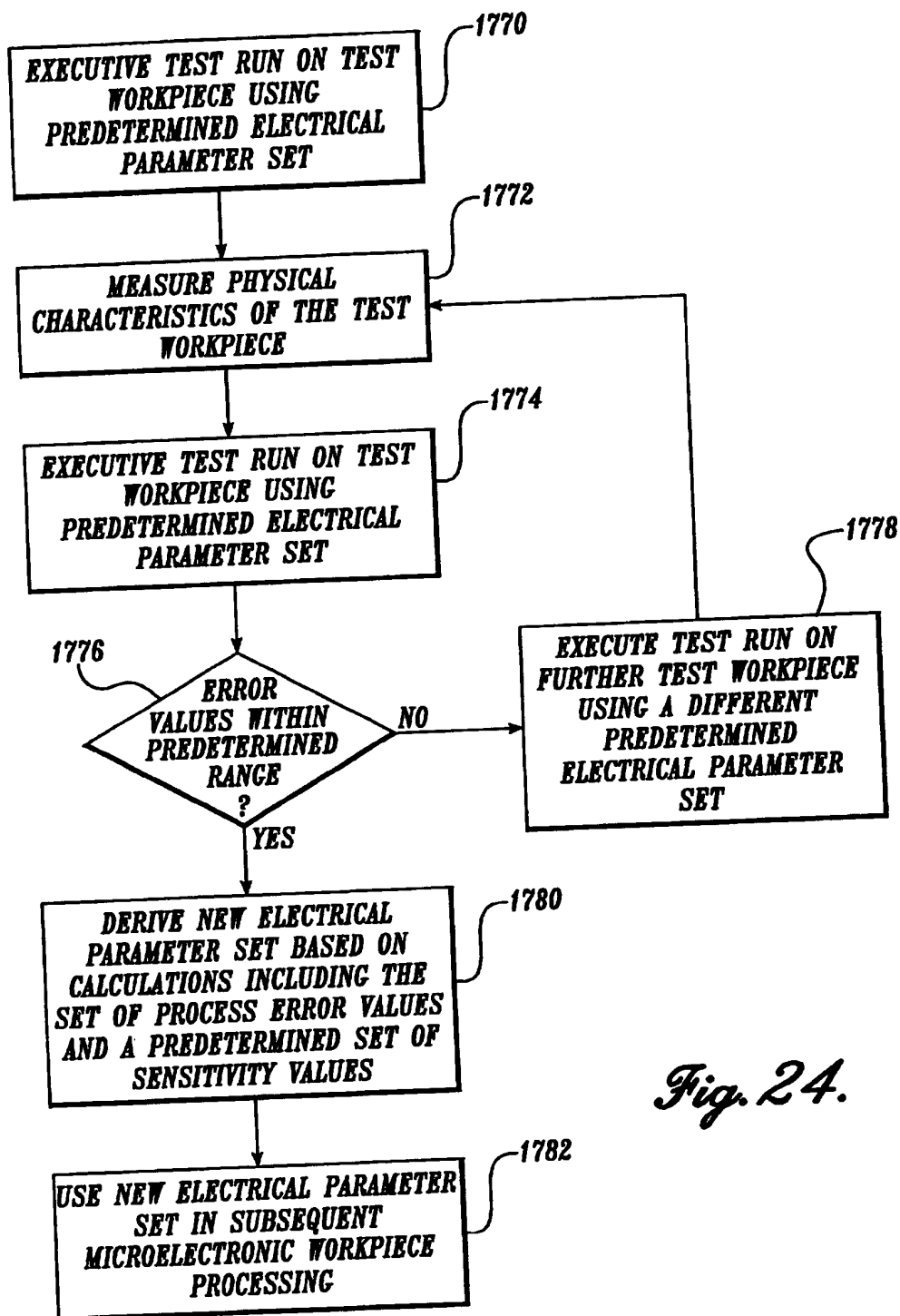


Fig. 24.

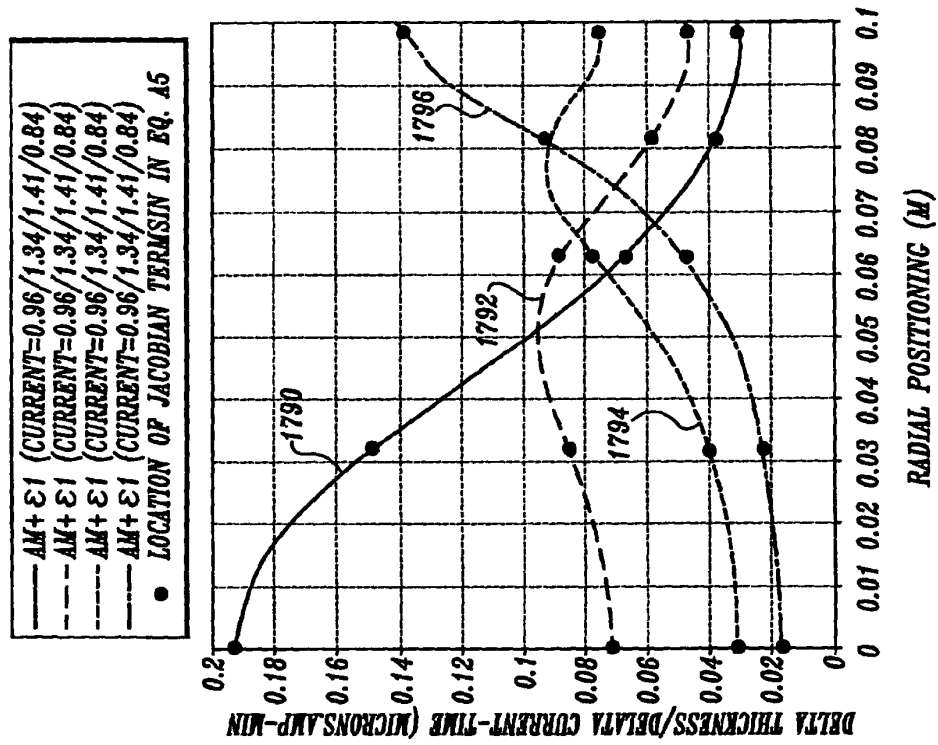


Fig. 25.

APPARATUS AND METHOD FOR ELECTROCHEMICALLY DEPOSITING METAL ON A SEMICONDUCTOR WORKPIECE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation of U.S. patent application No. 09/387,099, filed Aug. 31, 1999, which is a continuation of International Patent Application No. PCT/US99/06306, filed Mar. 22, 1999, designating the United States, which is a continuation-in-part of U.S. patent application No. 09/045,245, filed Mar. 20, 1998, and claiming the benefit of U.S. Provisional Patent Application No. 60/085,675, filed May 15, 1998; and is a continuation of International Patent Application No. PCT/US00/10120, filed Apr. 13, 2000, designating the United States and claiming the benefit of U.S. Provisional Patent Application Nos. 60/182,160, filed Feb. 14, 2000; 60/143,769, filed Jul. 12, 1999, and 60/129,055, filed Apr. 13, 1999; and claims the benefit of U.S. Provisional Patent Application No. 60/206,663, filed May 24, 2000, the disclosures of each of which are hereby expressly incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to electrochemical processing of workpieces, and particularly for processes, apparatus and chemical solutions for depositing metals on microelectronic and micromechanical workpieces.

BACKGROUND OF THE INVENTION

[0003] In the fabrication of microelectronic devices, application of one or more metallization layers is often an important step in the overall fabrication process. The metallization may be used in the formation of discrete microelectronic components, such as read/write heads, but it is more often used to interconnect components formed on a workpiece, such as a semiconductor workpiece. For example, such structures are used to interconnect the devices of an integrated circuit.

[0004] A basic understanding of certain terms used herein will assist the reader in understanding the disclosed subject matter. To this end, basic definitions of certain terms, as used in the present disclosure, are set forth below.

[0005] Single Metallization Level is defined as a composite level of a workpiece that is exterior to the substrate. The composite level comprises one or more metal structures.

[0006] Substrate is defined as a base layer of material over which one or more metallization levels are disposed. The substrate may be, for example, a semiconductor, a ceramic, etc.

[0007] Workpiece is defined as an object that at least comprises a substrate, and may include further layers of material or manufactured components, such as one or more metallization levels, disposed on the substrate. The workpiece may be, for example, a semiconductor wafer, a micromechanical device, or other device.

[0008] An integrated circuit is an interconnected ensemble of devices formed within a semiconductor material and

within a dielectric material that overlies a surface of the semiconductor. Devices which may be formed within the semiconductor include MOS transistors, bipolar transistors, diodes and diffused resistors. Devices which may be formed within the dielectric include thin-film resistors and capacitors. Typically, more than 100 integrated circuit die (IC chips) are constructed on a single 8 inch diameter silicon wafer. The devices utilized in each die are interconnected by conductor paths formed within the dielectric. Typically, two or more levels of conductor paths, with successive levels separated by a dielectric layer, are employed as interconnections. In current practice, an aluminum alloy and silicon oxide are typically used for, respectively, the conductor and dielectric.

[0009] Delays in propagation of electrical signals between devices on a single die limit the performance of integrated circuits. More particularly, these delays limit the speed at which an integrated circuit may process these electrical signals. Larger propagation delays reduce the speed at which the integrated circuit may process the electrical signals, while smaller propagation delays increase this speed. Accordingly, integrated circuit manufacturers seek ways in which to reduce the propagation delays.

[0010] For each interconnect path, signal propagation delay may be characterized by a time delay τ . See E.H. Stevens, *Interconnect Technology*, QMC, Inc., July 1993. An approximate expression for the time delay, τ , as it relates to the transmission of a signal between transistors on an integrated circuit is given below.

$$\tau = RC[1 + (V_{SAT}/RI_{SAT})]$$

[0011] In this equation, R and C are, respectively, an equivalent resistance and capacitance for the interconnect path and I_{SAT} and V_{SAT} are, respectively, the saturation (maximum) current and the drain-to-source potential at the onset of current saturation for the transistor that applies a signal to the interconnect path. The path resistance is proportional to the resistivity, ρ , of the conductor material. The path capacitance is proportional to the relative dielectric permittivity, K_e , of the dielectric material. A small value of τ requires that the interconnect line carry a current density sufficiently large to make the ratio V_{SAT}/RI_{SAT} small. It follows therefore, that a low- ρ conductor which can carry a high current density and a low- K_e dielectric must be utilized in the manufacture of high-performance integrated circuits.

[0012] To meet the foregoing criterion, copper interconnect lines within a low- K_e dielectric will likely replace aluminum-alloy lines within a silicon oxide dielectric as the most suitable interconnect structure. See "Copper Goes Mainstream: Low-k to Follow", *Semiconductor International*, November 1997, pp. 67-70. Resistivities of copper films are in the range of 1.7 to 2.0 $\mu\Omega\text{cm}$; resistivities of aluminum-alloy films are in the range of 3.0 to 3.5 $\mu\Omega\text{cm}$.

[0013] Despite the advantageous properties of copper, it has not been as widely used as an interconnect material as one would expect. This is due, at least in part, to the difficulty of depositing copper metallization and, further, due to the need for the presence of barrier layer materials. The need for a barrier layer arises from the tendency of copper to diffuse into silicon junctions and alter the electrical characteristics of the semiconductor devices formed in the substrate. Barrier layers made of, for example, titanium

nitride, tantalum nitride, etc., must be laid over the silicon junctions and any intervening layers prior to depositing a layer of copper to prevent such diffusion.

[0014] A number of processes for applying copper metallization to semiconductor workpieces have been developed in recent years. One such process is chemical vapor deposition (CVD), in which a thin copper film is formed on the surface of the barrier layer by thermal decomposition and/or reaction of gas phase copper compositions. A CVD process can result in conformal copper coverage over a variety of topological profiles, but such processes are expensive when used to implement an entire metallization layer.

[0015] Another known technique, physical vapor deposition (PVD), can readily deposit copper on the barrier layer with relatively good adhesion when compared to CVD processes. One disadvantage of PVD processes, however, is that they result in poor (non-conformal) step coverage when used to fill microstructures, such as vias and trenches, disposed in the surface of the semiconductor workpiece. For example, such non-conformal coverage results in less copper deposition at the bottom and especially on the sidewalls of trenches in the semiconductor devices.

[0016] Inadequate deposition of a PVD copper layer into a trench to form an interconnect line in the plane of a metallization layer is illustrated in FIG. 1. As illustrated, the upper portion of the trench is effectively "pinched off" before an adequate amount of copper has been deposited within the lower portions of the trench. This results in an open void region that seriously impacts the ability of the metallization line to carry the electrical signals for which it was designed.

[0017] Electrochemical deposition of copper has been found to provide the most cost-effective manner in which to deposit a copper metallization layer. In addition to being economically viable, such deposition techniques provide substantially conformal copper films that are mechanically and electrically suitable for interconnect structures. These techniques, however, are generally only suitable for applying copper to an electrically conductive layer. As such, an underlying conductive seed layer is generally applied to the workpiece before it is subject to an electrochemical deposition process. Techniques for electrodeposition of copper on a barrier layer material have not heretofore been commercially viable.

[0018] The present inventors have recognized that there exists a need to provide copper metallization processing techniques that 1) provide conformal copper coverage with adequate adhesion to the barrier layer, 2) provide adequate deposition speeds, and 3) are commercially viable. These needs are met by the apparatus and processes of the present invention as described below.

BRIEF SUMMARY OF THE INVENTION

[0019] The present invention provides processes and apparatus for enhancing or repairing ultra-thin or incomplete metal seed layers that have been deposited on a workpiece, using electrolytic or electroless plating baths, in an electrodeposition reactor that is designed and adaptable for substrates having differing electrical properties.

[0020] One embodiment of the invention provides a process for applying a metallization interconnect structure to a

workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer within a principal fluid chamber of a reactor to provide an enhanced seed layer using a second deposition process. The second deposition process, which is different from the first deposition process, entails supplying electroplating power to a plurality of concentric anodes disposed at different positions within the principal fluid flow chamber relative to the workpiece. After seed layer repair, additional metal is deposited in an electrolytic bulk plating process onto the enhanced seed layer, under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

[0021] Another embodiment of the invention provides a process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer within a principal fluid chamber of a reactor to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process. The second deposition process entails supplying electroplating power to a plurality of electrodes within the principal fluid flow chamber. At least two of the plurality of electrodes are independently connected to an electrical power supply. The supply of electrical power to the at least two electrodes is independently controlled during repair of the ultra-thin metal seed layer. After repair of the seed layer, additional metal is electrolytically deposited on the enhanced seed layer under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

[0022] Another embodiment of the invention provides a process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails subjecting the workpiece to an electrochemical deposition process that is different from the first deposition process, in an alkaline electroplating bath. The alkaline electroplating bath includes metal ions complexed with a complexing agent such that additional metal is deposited on the ultra-thin copper seed layer to thereby repair the seed layer. This results in an enhanced seed layer. The second deposition process is carried out by supplying electroplating power to a plurality of concentric anodes disposed at different positions, relative to the workpiece, within a principal fluid flow chamber of a reactor. Thereaf-

ter, additional metal is deposited on the enhanced seed layer using an electrolytic bulk deposition process under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

[0023] Another embodiment of the invention provides a process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails subjecting the workpiece to an electrochemical deposition process that is different from the first deposition process, in an alkaline electroplating bath. The bath includes metal ions complexed with a complexing agent such that additional metal is deposited on the ultra-thin copper seed layer to thereby repair the seed layer, resulting in an enhanced seed layer. The first deposition process entails supplying electroplating power to a plurality of electrodes within the principal fluid flow chamber, wherein at least two of the plurality of electrodes are independently connected to an electrical power supply. The supply of electrical power to the at least two electrodes is independently controlled during repair of the ultra-thin metal seed layer. Thereafter additional metal is electrolytically deposited on the enhanced seed layer under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

[0024] Another embodiment of the invention provides a process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer within a principal fluid chamber of a reactor to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process. During repair, the workpiece is exposed to an electroplating solution within a fluid flow chamber of a reactor. The fluid flow chamber defines a sidewall and a plurality of nozzles disposed in the sidewall and arranged and directed to provide vertical and radial fluid flow components that combine to create a substantially uniform normal flow component radially across a surface of the workpiece on which the ultra-thin metal seed layer is formed. Thereafter, additional metal is electrolytically deposited on the enhanced seed layer under conditions in which the deposition rate of the deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

[0025] Another embodiment of the invention provides a process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical

characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails subjecting the workpiece to an electrochemical deposition process that is different from the first deposition process, in an alkaline electroplating bath. The bath includes metal ions complexed with a complexing agent such that additional metal is deposited on the ultra-thin copper seed layer to thereby repair the seed layer, resulting in an enhanced seed layer. During repair, the workpiece is exposed to an electroplating solution within a fluid flow chamber of a reactor, the fluid flow chamber defining a sidewall and a plurality of nozzles disposed in the sidewall and arranged and directed to provide vertical and radial fluid flow components that combine to create a substantially uniform normal flow component radially across a surface of the workpiece on which the ultra-thin metal seed layer is formed. Thereafter, additional metal is deposited on the enhanced seed layer under electrolytic plating conditions in which the deposition rate of the deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

[0026] Another embodiment of the invention provides a process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer within a principal fluid chamber of a reactor to provide an enhanced seed layer using a second electrolytic or electroless deposition process, that is different from the first deposition process. Thereafter, additional metal is electrolytically deposited in bulk on the enhanced seed layer under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer. The bulk deposition process entails supplying electroplating power to a plurality of concentric anodes disposed at different positions within the principal fluid flow chamber relative to the workpiece.

[0027] Another embodiment of the invention provides a process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails repairing the ultra-thin metal seed layer by electrolytically or electrolessly depositing additional metal on the ultra-thin metal seed layer to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process. Thereafter, additional metal is electrolytically bulk deposited on the enhanced seed layer within a principal fluid chamber of a reactor under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer. The bulk deposition entails supplying electroplating power to a plurality of electrodes within the principal fluid flow chamber, wherein at least two of the plurality of

electrodes are independently connected to an electrical power supply. The supply of electrical power to the at least two electrodes is independently controlled during deposition.

[0028] Another embodiment of the invention provides a process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process. The first deposition process anchors the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal onto the metal seed layer. The process entails repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process. Thereafter, additional metal is electrochemically bulk deposited on the enhanced seed layer within a principal fluid chamber of a reactor under conditions in which the deposition rate of the deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer. The bulk deposition entails exposing the workpiece to an electroplating solution within a fluid flow chamber of a reactor, the fluid flow chamber defining a sidewall and a plurality of nozzles disposed in the sidewall and arranged and directed to provide vertical and radial fluid flow components that combine to create a substantially uniform normal flow component radially across a surface of the workpiece on which the ultra-thin metal seed layer is formed.

[0029] The present invention employs a novel approach to the metallization of a workpiece, such as a semiconductor workpiece. In accordance with the invention, an alkaline electroplating bath is suitably used to electroplate metal onto a seed layer, electroplate metal directly onto a barrier layer material, or repair (i.e., enhance) an ultra-thin copper seed layer which has been deposited on the barrier layer using a deposition process such as PVD or CVD. The metal deposition in the alkaline bath suitably takes place in a reactor including a plurality of electrodes. In a first embodiment the electrodes are concentric annular anodes arranged at differing positions relative to the workpiece. In a second embodiment, the plurality of electrodes are independently controlled for greater uniformity in metal deposition across the workpiece. In a third embodiment, the reactor is configured to induce a helical flow pattern in the plating bath solution during deposition.

[0030] The resulting metal layer provides an excellent conformal copper coating that fills trenches, vias, and other microstructures in the workpiece. When used for seed layer enhancement, the resulting metal seed layer provides an excellent conformal metal coating that allows the microstructures to be filled with a copper layer having good uniformity using electrochemical deposition techniques. Further, metal layers that are electroplated in the disclosed manner exhibit low sheet resistance and are readily annealed at low temperatures.

[0031] The disclosed process, as noted above, is applicable to a wide range of steps used in the manufacture of a metallization layer in a workpiece. The workpiece may, for example, be a semiconductor workpiece that is processed to form integrated circuits or other microelectronic compo-

nents, or a micromechanical device. Without limitation as to the applicability of the disclosed invention, a process for enhancing a seed layer is described.

[0032] A process for applying a metallization interconnect structure to a workpiece having a barrier layer deposited on a surface thereof is also set forth. The process includes the forming of an ultra-thin metal seed layer on the barrier layer. The ultra-thin seed layer has a thickness of less than or equal to about 500 Angstroms and may be formed from any material that can serve as a seed layer for subsequent metal deposition. Such metals include, for example, copper, copper alloys, aluminum, aluminum alloys, nickel, nickel alloys, zinc, chromium, tin, gold, silver, lead, cadmium, platinum, palladium, iridium and ruthenium, etc. The ultra-thin seed layer is then enhanced or repaired by depositing additional metal thereon in a separate deposition step to provide an enhanced seed layer that is suitable for use in a primary metal deposition. The metal deposition in the alkaline bath suitably takes place in a reactor including a plurality of electrodes. In a first embodiment the electrodes are concentric annular anodes arranged at differing positions relative to the workpiece. In a second embodiment, the plurality of electrodes are independently controlled for greater uniformity in metal deposition across the workpiece. In a third embodiment, the reactor is configured to induce a helical flow pattern in the plating bath solution during deposition. The enhanced seed layer has a thickness at all points on sidewalls of substantially all recessed features distributed within the workpiece that is equal to or greater than about 10% of the nominal seed layer thickness over an exteriorly disposed surface of the workpiece.

[0033] In accordance with a specific embodiment of the process, a copper-containing metallization interconnect structure is formed. To this end, the ultra-thin seed layer is enhanced or repaired by subjecting the semiconductor workpiece to an electrochemical copper deposition process in which an alkaline bath having a complexing agent is employed. The copper complexing agent may be at least one complexing agent selected from a group consisting of EDTA, ED, and a polycarboxylic acid such as citric acid or salts thereof.

[0034] In an alternate embodiment, the seed layer may be enhanced by using an electroless plating bath composition, such as an electroless copper sulfuric acid bath.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0035] FIG. 1 is a cross-sectional view illustrating an interconnect line formed completely by PVD copper.

[0036] FIGS. 2A-2E are cross-sectional views through a semiconductor workpiece illustrating the various layers of material as they are applied in accordance with one embodiment of the present invention.

[0037] FIG. 3 is a schematic representation of a first reactor suitable for enhancing an ultra-thin seed layer.

[0038] FIG. 4A is a graph illustrating the current-potential curves of a plating solution using a polycarboxylic acid, such as citric acid, as a complexing agent.

[0039] FIG. 4B is a graph illustrating the current-potential curves of a plating solution using EDTA, an amine-containing plating solution, as the complexing agent.

[0040] FIG. 4C is a graph of sheet resistance change with annealing temperature for copper films deposited from a bath solution with and without ammonium sulfate.

[0041] FIG. 4D is a graph illustrating plating solution conductivity as a function of ethylene glycol concentration in collating solutions with and without ammonium sulfate.

[0042] FIG. 5 is a scanning electromicrograph photograph illustrating an ultra-thin seed layer.

[0043] FIG. 6A is a scanning electromicrograph photograph illustrating an ultra-thin seed layer that has been enhanced in a citric acid bath.

[0044] FIG. 6B is a scanning electromicrograph photograph illustrating an ultra-thin seed layer that has been enhanced in an EDTA bath.

[0045] FIG. 7 is a schematic representation of a portion of a semiconductor manufacturing line suitable for implementing the disclosed seed layer enhancement steps.

[0046] FIG. 8 is a cross-sectional view of another embodiment of an electroplating reactor assembly that may incorporate the present invention.

[0047] FIG. 9 is a schematic diagram of one embodiment of a reactor chamber that may be used in the reactor assembly of FIG. 8 and includes an illustration of the velocity flow profiles associated with the flow of processing fluid through the reactor chamber.

[0048] FIGS. 10A, 10B, 11 and 12 illustrate a specific construction of a complete processing chamber assembly that has been specifically adapted for electrochemical processing of a semiconductor wafer and that has been implemented to achieve the velocity flow profiles set forth in FIG. 9.

[0049] FIGS. 13 and 14 illustrate a complete processing chamber assembly that has been constructed in accordance with a further embodiment of the present invention.

[0050] FIGS. 15 and 16 are a cross-sectional views of illustrative velocity flow contours of the processing chamber embodiment of FIGS. 13 and 14.

[0051] FIGS. 17 and 18 are graphs illustrating the manner in which the anode configuration of the processing chamber may be employed to achieve uniform plating.

[0052] FIGS. 19 and 20 illustrate a modified version of the processing chamber of FIGS. 13 and 14.

[0053] FIGS. 21 and 22 illustrate two embodiments of processing tools that may incorporate one or more processing stations constructed in accordance with the teachings of the present invention.

[0054] FIG. 23 is schematic block diagram of an electrochemical processing system constructed in accordance with one embodiment of the present invention.

[0055] FIG. 24 is a flowchart illustrating one manner in which the system of FIG. 23 can use a predetermined set of sensitivity values to generate a more accurate electrical parameter set for use in meeting targeted physical characteristics in the processing of a microelectronic workpiece.

[0056] FIG. 25 is a graph of the change in electroplated film thickness per change in current-time as a function of

radial position on a microelectronic workpiece for each of a plurality of individually controlled anodes, such as those shown at A1-A4 of FIG. 23.

DETAILED DESCRIPTION OF THE INVENTION

[0057] The present invention employs a novel approach to applying copper metallization to a workpiece, such as a semiconductor workpiece. In accordance with the invention, an alkaline electrolytic or electroless bath containing a metal ion to be deposited, such as an alkaline electrolytic copper bath, is used to electroplate metal onto a seed layer, electroplate metal directly onto a barrier layer material, or enhance or repair an ultra-thin metal seed layer which has been deposited on the barrier layer using a deposition process such as CVD or PVD. After enhancement of the ultra-thin metal seed layer, additional metal is suitable deposited, under differing conditions onto the enhanced seed layer, in a bulk fill process.

[0058] The present invention pertains to processes for applying a metallization layer. Although the disclosed method may be used in connection with a substantial number of different metal compositions, the specific embodiment disclosed herein is directed to the application of a copper-containing metallization layer. To this end, an alkaline electrolytic copper bath is used to enhance an ultra-thin copper seed layer which has been deposited on a barrier layer using a deposition process such as PVD. The enhanced copper seed layer provides an excellent conformal copper coating that allows trenches and vias to be subsequently bulk filled with a copper layer having good uniformity using electrochemical deposition techniques.

[0059] The seed layer enhancement process, or the bulk fill process, or both processes, are suitably carried out in a reactor that includes a plurality of anodes. The plurality of anodes may be arranged concentrically, or may be individually controlled with respect to applied voltage potential or current, to effect the uniformity of metal deposition across the workpiece. The seed layer enhancement and/or the bulk fill may also be carried out in a reactor that includes one or more jets, through which process fluid is introduced into a reaction chamber. The jets are angularly disposed relative to a chamber sidewall to create vertical and radial fluid flow components that combine to provide a substantially uniform normal flow component radially across a surface of the workpiece on which the metal is deposited. These processes and reactors in which they are suitable carried out will be described subsequently herein below.

[0060] A cross-sectional view of a micro-structure, such as trench 5, that is to be filled with copper metallization is illustrated in FIG. 2A and will be used to describe the seed layer enhancement aspects of the present invention. As shown, a thin barrier layer 10 of, for example, titanium nitride or tantalum nitride is deposited over the surface of a semiconductor device or, as illustrated in FIG. 2A, over a layer of a dielectric 8, such as silicon dioxide. The barrier layer 10 acts to prevent the migration of copper to any semiconductor device formed in the substrate. Any of the various known techniques, such as CVD or PVD, can be used to deposit the barrier layer depending on the particular barrier material being used. Suitably, the thickness for the barrier layer is approximately 100 to 300 Angstroms.

[0061] After the deposition of the barrier layer, an ultra-thin copper seed layer 15 is deposited on the barrier layer 10. The resulting structure is illustrated in FIG. 2B. Suitably, the copper seed layer 15 is formed using a vapor deposition technique, such as CVD or PVD. In order to have adequate adhesion and copper coverage, a relatively thick (1000 Angstroms) copper seed layer is usually required.

[0062] Such a thick seed layer leads to problems with close-off of small geometry trenches, however, when a PVD deposition process is employed for applying the seed layer. Contrary to traditional thoughts regarding seed layer application, the copper seed layer 15 of the illustrated embodiment is ultra-thin, having a thickness of about 50 to about 500 Angstroms, suitably about 100 to about 250 Angstroms, and still more suitably about 200 Angstroms. The ultra-thin copper seed layer can be deposited using a CVD or a PVD process, or a combination of both. PVD is the preferred application process, however, because it can readily deposit copper on the barrier layer 10 with relatively good adhesion. By depositing an ultra-thin seed layer of copper, rather than the relatively thick seed layer used in the prior art, pinching off of the trenches can be avoided.

[0063] The use of an ultra-thin seed layer 15 generally introduces its own set of problems. One of the most significant of these problems is the fact that such ultra-thin layers do not generally coat the barrier layer 10 in a uniform manner. Rather, voids or non-continuous seed layer regions on the sidewalls, such as at 20, are often present in an ultra-thin seed layer 15 thereby resulting in the inability to properly apply a subsequent electrochemically deposited copper layer in the regions 20. Further, ultra-thin seed layers tend to include spikes, such as at 21, that impact the uniformity of the subsequent electrolytically deposited metal layer. Such spikes 21 result in high potential regions at which the copper deposits at a higher rate than at other, more level regions. As such, the seed layer 15 is not fully suitable for the traditional electroplating techniques typically used after application of a seed layer.

[0064] The present inventors have found that an ultra-thin seed layer can be employed if it is combined with a subsequent electrochemical seed layer enhancement technique. In a first embodiment, the electrochemical enhancement technique is an electroplating technique using an alkaline plating bath. An alternate embodiment of electrochemical deposition to enhance or repair an ultra-thin or otherwise incomplete or deficient seed layer uses an electroless plating bath. Electroless plating baths are well known in the art, such as electroless copper sulfuric acid baths, and are used in accordance with the present invention to deposit additional metal on the initial ultra-thin seed layer to repair or enhance the seed layer.

[0065] The preferred technique of electroplating in an alkaline bath to repair or enhance a seed layer will now be described. To this end, the semiconductor workpiece is subject to a subsequent process step in which a further amount of copper 18 is applied to the ultra-thin seed layer to thereby enhance the seed layer. A seed layer enhanced by the additional deposition of copper is illustrated in FIG. 2C. As shown in FIG. 2C, the void or non-continuous regions 20 of FIG. 2B have been filled thereby leaving substantially all of the barrier layer 10 covered with copper.

[0066] Suitably, the seed layer enhancement process continues until a sidewall step coverage, i.e., the ratio of the

seed layer thickness at the bottom sidewall regions 22 to the nominal thickness of the seed layer at the exteriorly disposed side 23 of the workpiece, achieves a value of at least 10%. More suitably, the sidewall step coverage is at least about 20%. Such sidewall step coverage values are present in substantially all of the recessed structures of the semiconductor workpiece. It will be recognized, however, that certain recessed structures distributed within the semiconductor workpiece may not reach these sidewall step coverage values. For example, such structures disposed at the peripheral edges of a semiconductor wafer may not reach these step coverage values. Similarly, defects or contaminants at the situs of certain recessed structures may prevent them from reaching the desired coverage values. The nominal thickness of the enhanced seed layer at the exteriorly disposed side of the workpiece is suitably in the range of 500 angstroms 1600 angstroms.

[0067] Although the embodiment of the process disclosed herein is described in connection with copper metallization, it is understood that the basic principle of the enhancement of an ultra-thin seed layer prior to the bulk deposition thereof can be applied to other metals or alloys that are capable of being electroplated. Such metals include iron, nickel, cobalt, zinc, copper-zinc, nickel-iron, cobalt-iron, etc.

[0068] The embodiments disclosed above utilize depositing a metal, such as copper, during seed layer enhancement. It should be understood that alternately a metal alloy, such as a copper alloy may be applied. The alloy is suitably selected to include an element or elements that preferentially locate at the interfaces between differing materials, which enhances anchorage of the materials, and also may lead to improved electromigration effect.

[0069] A thermal processing step may also be employed after seed layer enhancement deposition, at an elevated temperature selected to cause material diffusion at the interfaces between materials, thereby anchoring the materials or components thereof together.

[0070] A schematic representation of a reactor 25 suitable for enhancing the ultra-thin copper seed layer is illustrated in FIG. 3. It will be recognized that this apparatus is also suitable for applying a blanket plating layer and/or full-fill plating of recessed micro-structures. As shown, a semiconductor workpiece, such as a semiconductor wafer 30, is positioned face down in a bath 35 of electroplating solution. One or more contacts 40 are provided to connect the wafer 30 to a plating power supply 45 as a cathode of an electroplating cell. An anode 50 is disposed in the bath 35 and is connected to the plating power supply 45. Suitably, a diffuser 55 is disposed between the anode 50 and the wafer/cathode 30. The wafer 30 may be rotated about axis 60 during the enhancement process. Anode 50 may be provided with a dielectric shield 65 at a backside thereof which faces an incoming stream of plating bath fluid. Alternate and preferred reactors for use in the present invention will be described subsequently herein below.

[0071] A. Electroplating Solutions And Processes

[0072] As noted above, certain aspects of the present invention relate to new and useful plating solutions. These solutions can be used for blanket plating, full-fill of the recessed micro-structures, seed layer enhancement, etc. The preferred electrolytic bath solution for enhancing the seed

layer is an alkaline copper bath in which copper ions are complexed with a complexing agent. A suitable composition and range of concentrations for the various components of the plating bath include the following:

- [0073] 1. Copper sulfate: 0.03M to 0.25M (suitably, 0.04);
- [0074] 2. Complexing agent: complex to metal ratios from 1 to 4, suitably 2;
- [0075] 3. Boric acid: 0.01M to 0.5M, suitably 0.05M; and
- [0076] 4. pH: 5 -13, suitably 9.5.

[0077] A suitable source of copper ions is copper sulfate (CuSO_4). The concentration of copper sulfate in the bath is suitably within the range of 0.03 to 0.25 M, and is more suitably about 0.1 M.

[0078] Complexing agents that are suitable for use in the present invention form a stable complex with copper ions and prevent the precipitation of copper hydroxide. Ethylene diamine tetracetic acid (EDTA), ethylene diamine (ED), citric acid, and their salts have been found to be particularly suitable copper complexing agents. The molar ratio of complexing agent to copper sulfate in the bath is suitably within the range of 1 to 4, and is suitably about 2. Such complexing agents can be used alone, in combination with one another, or in combination with one or more further complexing agents.

[0079] The electrolytic bath is suitably maintained at a pH of at least 9.0. Potassium hydroxide, ammonium hydroxide, tetramethylammonium hydroxide, or sodium hydroxide is utilized to adjust and maintain the pH at the desired level of 9.0 or above. A suitable pH for a citric acid or ED bath is about 9.5, while a suitable pH for an EDTA bath is about 12.5. As noted above, the complexing agent assists in preventing the copper from precipitating at the high pH level.

[0080] Additional components can be added to the alkaline copper bath. For example, boric acid (H_3BO_3) aids in maintaining the pH at 9.5 when citric acid or ED is used as the complexing agent, and provides brighter copper deposits when added to an electrolytic bath containing EDTA as the complexing agent. If boric acid is added, its concentration in the bath is suitably within the range of 0.01 to 0.5 M.

[0081] In general, the temperature of the bath can be within the range of 20 to 35° C., with 25° C. being a suitable temperature. The current density for electrolytically depositing copper to enhance the copper seed layer can be 1 to 5 milliamperes/cm², while a plating time of about 1 to about 5 minutes is sufficient to enhance the copper seed layer. The plating waveform may be, for example, a forward periodic pulse having a period of 2 msec at a 50% duty cycle.

[0082] An amine free acid complexing agent, for example, a polycarboxylic acid, such as citric acid, and salts thereof, is preferable to the use of EDTA or ED. EDTA and ED include amine groups. These amine groups often remain on the surface of the semiconductor workpiece after rinsing and drying of the wafer. Subsequent processes, particularly such processes as photolithographic processes, may be corrupted by the reactions resulting from the presence of these amine groups. The amine groups may, for example, interfere with

the chemical reactions associated with the exposing and/or curing of photoresist materials. As such, amine free complexing agents are particularly suitable in processes in which a photolithographic process follows an electrodeposition process.

[0083] A further advantage of using a polycarboxylic acid, such as citric acid, stems from the fact that the magnitude of the voltage potential at which the copper is plated is greater than the magnitude of the voltage potential at which the copper is plated in a bath containing EDTA. This is illustrated in FIGS. 4A and 4B where FIG. 4A is a current-potential graph for a citric acid bath, and FIG. 4B is a current-potential graph for an EDTA bath. Electroplating takes place at the voltage where the corresponding current increases abruptly. This plating voltage is referred to as the deposition potential, which is approximately -1.25 volts as shown in FIG. 4A for a bath employing citric acid as the complexing agent, and is approximately -1.0 volts as shown in FIG. 4B for a bath employing EDTA as the complexing agent. The current peaks (70'70' for the bath containing a citric acid, and 72, 72' for the bath containing the EDTA) are the limiting currents which are mainly determined by mass transfer and the concentration of copper ions in the plating solutions. As illustrated, the magnitude of the current and the particular plating potential is slightly dependent on the substrate material. The different substrate results are illustrated in FIGS. 4A and 4B, where 70 and 72 are the curves for a copper substrate material, and 70' and 72' are curves for a copper substrate material comprised of copper with a copper oxide coating. It is noted that additional peaks occur on oxidized copper in the same electrolytes. These peaks are related to the electrochemical reduction of copper oxide to metallic copper before the alkaline electrochemical copper deposition.

[0084] It is believed that a copper layer plated at a higher plating potential in an alkaline bath provides greater adhesion to the underlying barrier layer than a copper layer plated at a lower plating potential in an acid bath. For copper to adhere to the barrier material, it is thought that copper ions must impinge on the barrier surface with sufficient energy to penetrate a thin oxidized or contaminated layer at the barrier surface. It is therefore believed that a copper layer deposited at a higher magnitude plating potential adheres better to the exposed barrier layer during the plating process when compared to a layer plated using a smaller magnitude plating potential. This factor, combined with the inter-copper chemical bond between the PVD copper and the electrochemically deposited copper provides for an enhanced seed layer having excellent electrical as well as barrier adhesion properties. Such characteristics are also desirable for films used in blanket plating, full-fill plating, pattern plating, etc.

[0085] It has been found that the resistivity of the deposited copper film is directly related to the resistivity of the plating bath solution. Additives that assist in lowering the resistivity of the solution therefore provide a corresponding reduction in the resistivity of the deposited film.

[0086] Experimental results indicate that addition of ammonium sulfate significantly reduces the resistivity of the plating bath solution and, as such, the deposited film. The sheet resistance obtained for different amounts of ammonium sulfate are compared in the graph FIG. 4C. As can be seen, the highest sheet resistance, either with or without

annealing at high temperatures, was obtained in the bath containing no ammonium sulfate. If ammonium hydroxide was used to adjust pH in which a trace amount of ammonium sulfate is introduced to the bath, the sheet resistance was reduced from 76 to 23. As the concentration of ammonium sulfate increased from 0.1 M to 0.5 M, the sheet resistance continuously decreased in a corresponding manner.

[0087] Although ammonium sulfate assists in reducing the sheet resistance of the deposited copper layer, experimental results indicate that it reduces the conformality of the resulting copper film. However, the addition of ethylene glycol to the ammonium sulfate containing solution substantially increases the conformality of the resulting deposit. FIG. 4D illustrates the relationship between the concentration of ethylene glycol and the conductivity of a plating solution containing 0.2M the of ammonium sulfate.

[0088] A suitable composition and range of concentrations for the various components of a plating bath having ammonium sulfate include the following:

- [0089] 1. Copper sulfate: 0.03M to 0.5M (suitably, 0.25M);
- [0090] 2. Complexing agent: complex to metal ratios from 1 to 4, suitably 2 using ED;
- [0091] 3. Ammonium sulfate: 0.01M to 0.5M, suitably 0.3M; and
- [0092] 4. Boric acid: 0.00 to 0.5M, suitably 0.2M.

[0093] As noted above, such a bath composition can be used for blanket plating, pattern plating, full-fill plating, and seed layer enhancement.

[0094] With reference again to the specific seed layer enhanced aspects of the present invention, the enhanced seed layer of FIG. 2C is suitable for subsequent electrochemical copper deposition. This subsequent copper deposition may take place in an alkaline bath within the apparatus employed to enhance the seed layer. This may be followed by a low-temperature annealing process that assists in lowering the resistivity of the deposited copper. Such a low-temperature annealing process suitably takes place at a temperature below about the 250 degrees Celsius and, more suitably, below about 100 degrees Celsius. When a low-K dielectric material is employed to isolate the copper structures, the upper annealing temperature limit should be chosen to be below the degradation temperature of the dielectric material.

[0095] Although the foregoing alkaline bath compositions may be used for the entire electrochemical deposition process, subsequent copper deposition suitably takes place in an acid environment where plating rates are substantially higher than corresponding rates associated with alkaline plating baths. To this end, the semiconductor workpiece is suitably transferred to an apparatus wherein the workpiece is thoroughly rinsed with deionized water and then transferred to an apparatus similar to that of FIG. 3 wherein the plating bath is acidic. For example, one suitable copper bath comprises 170 g/l H_2SO_4 , 17 g/l copper and 70 ppm Chloride ions with organic additives. The organic additives are not absolutely necessary to the plating reaction. Rather, the organic additives may be used to produce desired film characteristics and provide better filling of the recessed structures on the wafer surface. The organic additives may include levelers, brighteners, wetting agents and ductility

enhancers. It is during this deposition process that the trench 5 is substantially filled with a further layer of electrochemically deposited copper 22. The resulting filled cross-section is illustrated in FIG. 2D. After being filled in this manner, the barrier layer and the copper layers disposed above the trench are removed using any suitable process thereby leaving only the trench 5 with the copper metallization and associated barrier material as shown in FIG. 2E.

[0096] While electrolytic seed layer enhancement is an embodiment of the present invention, the ultra-thin seed layer can alternately be enhanced in accordance with the present invention using an electroless plating bath solution containing metal ions to be deposited. Electroless plating baths are well known. The workpiece with ultra-thin seed layer is immersed in the electroless bath, or electroless bath solution is otherwise applied to the workpiece, for a predetermined time period sufficient to deposit additional metal ions to enhance the seed layer, rendering it suitable for metal deposition at a higher rate.

[0097] Use of an alkaline electrolytic bath to enhance the copper seed layer has particular advantages over utilizing acid copper baths without seed layer enhancement. After deposition of the PVD copper seed layer, the copper seed layer is typically exposed to an oxygen-containing environment. Oxygen readily converts metallic copper to copper oxide. If an acid copper bath is used to plate copper onto the seed layer after exposure of the seed layer to an oxygen containing environment, the acid copper bath would dissolve copper oxide that had formed, resulting in voids in the seed layer and poor uniformity of the copper layer deposited on the seed layer. Use of an alkaline copper bath in accordance with the disclosed embodiment avoids the problem by advantageously reducing any copper oxide at the surface of the seed layer to metallic copper. Another advantage of the alkaline copper bath is that the plated copper has much better adhesion to the barrier layer than that plated from an acid copper bath. Additional advantages of the seed layer enhancement aspects of the present invention can be seen from the following Example.

EXAMPLE 1

Comparison of Acid Copper Plating With and Without Seed Layer Enhancement

[0098] Semiconductor wafers 1, 2 and 3 were each coated with a 200 Angstrom PVD copper seed layer. In accordance with the present invention, wafers 1 and 2 had seed layer enhancement from citric acid and EDTA baths, respectively, the compositions of which are set forth below:

[0099] Bath for Wafer 1: 0.1 M $Cu SO_4 + 0.2$ M Citric acid + 0.05 M H_3BO_3 in D.I. water at pH 9.5, temperature 25° C.

[0100] Bath for Wafer 2: 0.1 M $Cu SO_4 + 0.2$ M EDTA acid + 0.05 H_3BO_3 in D.I. water at pH 12.5, temperature 25° C.

[0101] Wafer 3 did not have any seed layer enhancement.

[0102] The three wafers were then plated with a 1.5 micron copper layer from an acid copper bath under identical conditions. The following Table compares the uniformities, as deduced from sheet resistance measurements, of

the three wafers after the deposition of a copper layer having a nominal thickness of 1.5 microns.

TABLE 1

Wafer	Enhancement Bath	Current Density	Non-uniformity Standard deviation (% , 1 σ)
1	Citrate	3 min. at 2 mA/cm ²	7.321
2	EDTA	3 min. at 2 mA/cm ²	6.233
3	None	0	46.10

[0103] As can be seen from the results in Table 1 above, seed layer enhancement in accordance with the disclosed process provides excellent uniformity (6 to 7%) compared to that without seed layer enhancement (46%). This is consistent with observations during visual examination of the wafer after 1.5 micron electroplated copper had been deposited. Such visual examination of the wafer revealed the presence of defects at wafer electrode contact points on the wafer without seed layer enhancement.

[0104] FIGS. 5, 6A and 6B are photographs taken using a SEM. In FIG. 5, an ultra-thin seed layer has been deposited on the surface of a semiconductor wafer, including microstructures, such as trenches 85. As shown, void regions are present at the lower corners of the trenches. In FIG. 6A, the seed layer has been enhanced in the manner described above in a bath containing citric acid as the complexing agent. This enhancement resulted in a conformal copper seed layer that is very suited for subsequent electrochemical deposition of copper metallization.

[0105] FIG. 6B illustrates a seed layer that has been enhanced in a bath containing EDTA as the complexing agent. The resulting seed layer includes larger grain sizes that project as spikes from the sidewalls of the trenches. These sidewall grain projections make subsequent electrochemical deposition filling of the trenches more difficult since they localize a higher plating rate resulting in non-uniformity of the subsequent electrochemical deposition. This effect is particularly noticeable in recessed microstructures having small dimensions. As such, a complexing agent such as citric acid is more preferable when filling small microstructures. Results comparable for copper baths containing citric acid have also been achieved using ED as the complexing agent.

[0106] B. Electrodeposition System

[0107] FIG. 7 is a schematic representation of a portion of a semiconductor manufacturing line 90 suitable for implementing the foregoing processes. The line 90 includes a vapor deposition tool or tool set 95 and an electrochemical copper deposition tool or tool set 100. Transfer of wafers between the tools/tool sets 95 and 100 may be implemented manually or through an automated transfer mechanism 105. Suitably, automated transfer mechanism 105 transfers workpieces in a pod or similar environment. Alternatively, the transfer mechanism 105 may transfer wafers individually or in an open carrier through a clean atmosphere joining the tools/tool sets.

[0108] In operation, vapor deposition tool/tool set 95 is utilized to apply an ultra-thin copper seed layer over at least

portions of semiconductor workpieces that are processed on line 90. Suitably, this is done using a PVD application process. Workpieces with the ultra-thin seed layer are then transferred to tool/tool set 100, either individually or in batches, where they are subject to electrochemical seed layer enhancement at, for example, processing station 110. For electrolytic seed layer enhancement, processing station 110 may be constructed in the manner set forth in FIG. 3. For electroless enhancement, a similar processing station 110 will be utilized, but electrical contact is not made with the workpiece and voltage is not applied. After enhancement is completed, the workpieces are subject to a full electrochemical deposition process in which copper metallization is applied to the workpiece to a desired interconnect metallization thickness. This latter process may take place at station 110, but suitably occurs at further processing station 115 which deposits the copper metallization in the presence of an acidic plating bath. Before transfer to station 115, the workpiece is suitably rinsed in DI water at station 112. Transfer of the wafers between stations 110, 112, and 115 may be automated by a wafer conveying system 120. The electrochemical deposition tool set 100 may be implemented using, for example, an LT-210™ model or an Equinox™ model plating tool available from Semitool, Inc., of Kalispell, Mont.

[0109] C. Suitable Reactor For Seed Layer Enhancement

[0110] With reference to FIG. 8, a first reactor assembly 120 for electroplating a microelectronic workpiece 125, such as a semiconductor wafer, is shown. Generally stated, the reactor assembly 120 is comprised of a reactor head 130 and a corresponding reactor base, shown generally at 137 and described in substantial detail below, in which the electroplating solution is disposed. The reactor of FIG. 8 can also be used to implement electrochemical processing operations other than electroplating (e.g., electropolishing, anodization, etc.), and also electroless deposition processes.

[0111] The reactor head 130 of the electroplating reactor assembly may comprised of a stationary assembly 170 and a rotor assembly 175. Rotor assembly 175 is configured to receive and carry an associated microelectronic workpiece 125, position the microelectronic workpiece in a process-side down orientation within a container of reactor base 137, and to rotate or spin the workpiece while joining its electrically-conductive surface in the plating circuit of the reactor assembly 120. The rotor assembly 175 includes one or more cathode contacts (when used for electrolytic processing) that provide electroplating power to the surface of the microelectronic workpiece. In the illustrated embodiment, a cathode contact assembly is shown generally at 185 and is described in further detail below. It will be recognized, however, that backside contact may be implemented in lieu of front side contact when the substrate is conductive or when an alternative electrically conductive path is provided between the back side of the microelectronic workpiece and the front side thereof.

[0112] The reactor head 130 is typically mounted on a lift/rotate apparatus which is configured to rotate the reactor head 130 from an upwardly-facing disposition in which it receives the microelectronic workpiece to be plated, to a downwardly facing disposition in which the surface of the microelectronic workpiece to be plated is positioned so that it may be brought into contact with the electroplating

solution in reactor base 137, either planar or at a given angle. A robotic arm, which suitably includes an end effector, is typically employed for placing the microelectronic workpiece 125 in position on the rotor assembly 175, and for removing the plated microelectronic workpiece from within the rotor assembly. The contact assembly 185 may be operated between an open state that allows the microelectronic workpiece to be placed on the rotor assembly 175, and a closed state that secures the microelectronic workpiece to the rotor assembly and brings the electrically conductive components of the contact assembly 185 into electrical engagement with the surface of the microelectronic workpiece that is to be plated.

[0113] It will be recognized that other reactor assembly configurations may be used with the inventive aspects of the disclosed reactor chamber, the foregoing being merely illustrative.

[0114] FIG. 9 illustrates the basic construction of processing base 137 and a corresponding computer simulation of the flow velocity contour pattern resulting from the processing container construction. As illustrated, the processing base 137 generally comprises a main fluid flow chamber 505, an antechamber 510, a fluid inlet 515, a plenum 520, a flow diffuser 525 separating the plenum 520 from the antechamber 510, and a nozzle/slot assembly 530 separating the plenum 520 from the main chamber 505. These components cooperate to provide a flow of electrochemical processing fluid (here, of the electroplating solution) at the microelectronic workpiece 125 that has a substantially radially independent normal component. In the illustrated embodiment, the impinging flow is centered about central axis 537 and possesses a nearly uniform component normal to the surface of the microelectronic workpiece 125. This results in a substantially uniform mass flux to the microelectronic workpiece surface that, in turn, enables substantially uniform processing thereof, for example, when used to introduce an alkaline bath solution for seed layer enhancement.

[0115] Notably, as will be clear from the description below, this desirable flow characteristic is achieved without the use of a diffuser disposed between the anode(s) and surface of the microelectronic workpiece that is to be electrochemically processed (e.g., electroplated). As such, the anodes used in the electroplating reactor can be placed in close proximity to the surface of the microelectronic workpiece to thereby provide substantial control over local electrical field/current density parameters used in the electroplating process. This substantial degree of control over the electrical parameters allows the reactor to be readily adapted to meet a wide range of electroplating requirements (e.g., seed layer thickness, seed layer type, electroplated material, electrolyte bath properties, etc.) without a corresponding change in the reactor hardware. Rather, adaptations can be implemented by altering the electrical parameters used in the electroplating process through, for example, software control of the power provided to the anodes, as shall be described further herein below.

[0116] The reactor design thus effectively de-couples the fluid flow from adjustments to the electric field. An advantage of this approach is that a chamber with nearly ideal flow for electroplating and other electrochemical processes (i.e., a design which provides a substantially uniform diffusion

layer across the microelectronic workpiece) may be designed that will not be degraded when electroplating or other electrochemical process applications require significant changes to the electric field.

[0117] The foregoing advantages can be more greatly appreciated through a comparison with the conventional prior art reactors. In such conventional designs, the diffuser must be moved closer to the surface of the workpiece if the distance between the anode and the workpiece surface is to be reduced. However, moving the diffuser closer to the workpiece significantly alters the flow characteristics of the electroplating fluid at the surface of the workpiece. More particularly, the close proximity between the diffuser and the surface of the workpiece introduces a corresponding increase in the magnitude of the normal components of the flow velocity at local areas 9. As such, the anode cannot be moved so that it is in close proximity to the surface of the microelectronic workpiece that is to be electroplated without introducing substantial diffusion layer control problems and undesirable localized increases in the electrical field corresponding to the pattern of apertures in the diffuser. Since the anode cannot be moved in close proximity to the surface of the microelectronic workpiece, the advantages associated with increased control of the electrical characteristics of the electrochemical process cannot be realized. Still further, movement of the diffuser to a position in close proximity with the microelectronic workpiece effectively generates a plurality of virtual anodes defined by the hole pattern of the diffuser. Given the close proximity of these virtual anodes to the microelectronic workpiece surface, the virtual anodes have a highly localized effect. This highly localized effect cannot generally be controlled with any degree of accuracy given that any such control is solely effected by varying the power to the single, real anode. A substantially uniform electroplated film is thus difficult to achieve with such a plurality of loosely controlled virtual anodes.

[0118] With reference again to FIG. 9, electroplating solution is provided through inlet 515 disposed at the bottom of the base 137. The fluid from the inlet 515 is directed therefrom at a relatively high velocity through antechamber 510. In the illustrated embodiment, antechamber 510 includes an acceleration channel 540 through which the electroplating solution flows radially from the fluid inlet 515 toward fluid flow region 545 of antechamber 510. Fluid flow region 545 has a generally inverted U-shaped cross-section that is substantially wider at its outlet region proximate flow diffuser 525 than at its inlet region proximate channel 540. This variation in the cross-section assists in removing any gas bubbles from the electroplating solution before the electroplating solution is allowed to enter the main chamber 505. Gas bubbles that would otherwise enter the main chamber 505 are allowed to exit the processing base 137 through a gas outlet (not illustrated in FIG. 9, but illustrated in the embodiment shown in FIGS. 10-12) disposed at an upper portion of the antechamber 510.

[0119] Electroplating solution within antechamber 510 is ultimately supplied to main chamber 505. To this end, the electroplating solution is first directed to flow from a relatively high-pressure region 550 of the antechamber 510 to the comparatively lower-pressure plenum 520 through flow diffuser 525. Nozzle assembly 530 includes a plurality of nozzles or slots 535 that are disposed at a slight angle with respect to horizontal. Electroplating solution exits plenum

520 through nozzles 535 with fluid velocity components in the vertical and radial directions.

[0120] Main chamber 505 is defined at its upper region by a contoured sidewall 560 and a slanted sidewall 565. The contoured sidewall 560 assists in preventing fluid flow separation as the electroplating solution exits nozzles 535 (particularly the uppermost nozzle(s)) and turns upward toward the surface of microelectronic workpiece 125. Beyond breakpoint 570, fluid flow separation will not substantially affect the uniformity of the normal flow. As such, sidewall 565 can generally have any shape, including a continuation of the shape of contoured sidewall 560. In the specific embodiment disclosed here, sidewall 565 is slanted and, as will be explained in further detail below, is used to support one or more anodes.

[0121] Electroplating solution exits from main chamber 505 through a generally annular outlet 572. Fluid exiting outlet 572 may be provided to a further exterior chamber for disposal or may be replenished for re-circulation through the electroplating solution supply system.

[0122] The processing base 137 is also provided with one or more anodes. In the illustrated embodiment, a principal anode 580 is disposed in the lower portion of the main chamber 505. If the peripheral edges of the surface of the microelectronic workpiece 125 extend radially beyond the extent of contoured sidewall 560, then the peripheral edges are electrically shielded from principal anode 580 and reduced plating will take place in those regions. As such, a plurality of annular anodes 585 are disposed in a generally concentric manner on slanted sidewall 565 to provide a flow of electroplating current to the peripheral regions.

[0123] Anodes 580 and 585 of the illustrated embodiment are disposed at different distances from the surface of the microelectronic workpiece 125 that is being electroplated. More particularly, the anodes 580 and 585 are concentrically disposed in different horizontal planes. Such a concentric arrangement combined with the vertical differences allow the anodes 580 and 585 to be effectively placed close to the surface of the microelectronic workpiece 125 without generating a corresponding adverse impact on the flow pattern as tailored by nozzles 535. The plurality of anodes illustrated are arranged at increasing distances from the workpiece from an innermost one of the concentric anodes to an outermost one of the concentric anodes. However, for differing deposition patterns, an alternate arrangement providing for the distance from anode to workpiece increasing from outermost to innermost is also within the scope of the present invention.

[0124] The effect and degree of control that an anode has on the electroplating of microelectronic workpiece 125 is dependent on the effective distance between that anode and the surface of the microelectronic workpiece that is being electroplated. More particularly, all other things being equal, an anode that is effectively spaced a given distance from the surface of microelectronic workpiece 125 will have an impact on a larger area of the microelectronic workpiece surface than an anode that is effectively spaced from the surface of microelectronic workpiece 125 by a lesser amount. Anodes that are effectively spaced at a comparatively large distance from the surface of microelectronic workpiece 125 thus have less localized control over the electroplating process than do those that are spaced at a

smaller distance. It is therefore desirable to effectively locate the anodes in close proximity to the surface of microelectronic workpiece 125 since this allows more versatile, localized control of the electroplating process. Advantage can be taken of this increased control to achieve greater uniformity of the resulting electroplated film. Such control is exercised, for example, by placing the electroplating power provided to the individual anodes under the control of a programmable controller or the like, as shall be described subsequently herein below. Adjustments to the electroplating power can thus be made subject to software control based on manual or automated inputs.

[0125] In the illustrated embodiment, anode 580 is effectively "seen" by microelectronic workpiece 125 as being positioned an approximate distance A1 from the surface of microelectronic workpiece 125. This is due to the fact that the relationship between the anode 580 and sidewall 560 creates a virtual anode having an effective area defined by the innermost dimensions of sidewall 560. In contrast, anodes 585 are approximately at effective distances A2, A3, and A4 proceeding from the innermost anode to the outermost anode, with the outermost anode being closest to the microelectronic workpiece 125. All of the anodes 585 are in close proximity (i.e., about 25.4 mm or less, with the outermost anode being spaced from the microelectronic workpiece by about 10 mm) to the surface of the microelectronic workpiece 125 that is being electroplated. Since anodes 585 are in close proximity to the surface of the microelectronic workpiece 125, they can be used to provide effective, localized control over the radial film growth at peripheral portions of the microelectronic workpiece. Such localized control is particularly desirable at the peripheral portions of the microelectronic workpiece since it is those portions that are more likely to have a high uniformity gradient (most often due to the fact that electrical contact is made with the seed layer of the microelectronic workpiece at the outermost peripheral regions resulting in higher plating rates at the periphery of the microelectronic workpiece compared to the central portions thereof).

[0126] The electroplating power provided to the foregoing anode arrangement can be readily controlled to accommodate a wide range of plating requirements without the need for a corresponding hardware modification. Some reasons for adjusting the electroplating power include changes to the following:

- [0127] seed layer thickness;
- [0128] open area of plating surface (pattern wafers, edge exclusion);
- [0129] final plated thickness;
- [0130] plated film type (copper, platinum, seed layer enhancement);
- [0131] bath conductivity, metal concentration; and
- [0132] plating rate.

[0133] The foregoing anode arrangement is particularly well-suited for plating microelectronic workpieces having highly resistive seed layers, for enhancing such highly resistive seed layers, and also for plating highly resistive materials on microelectronic workpieces. Generally stated, the more resistive the seed layer or material that is to be deposited, the more the magnitude of the current or potential

at the central anode 580 (or central anodes) should be increased to yield a uniform film. This effect can be understood in connection with an example and the set of corresponding graphs set forth in FIGS. 17 and 18.

[0134] FIG. 17 is a graph of four different computer simulations reflecting the change in growth of an electroplated film versus the radial position across the surface of a microelectronic workpiece. The graph illustrates the changing growth that occurs when the current to a given one of the four anodes 580, 585 is changed without a corresponding change in the current to the remaining anodes. In this illustration, Anode 1 corresponds to anode 580 and the remaining Anodes 2 through 4 correspond to anodes 585 proceeding from the interior most anode to the outermost anode. The peak plating for each anode occurs at a different radial position. Further, as can be seen from this graph, anode 580, being effectively at the largest distance from the surface of the workpiece, has an effect over a substantial radial portion of the workpiece and thus has a broad affect over the surface area of the workpiece. In contrast, the remaining anodes have substantially more localized effects at the radial positions corresponding to the peaks of the graph of FIG. 17.

[0135] The differential radial effectiveness of the anodes 580, 585 can be utilized to provide an effectively uniform electroplated film across the surface of the microelectronic workpiece. To this end, each of the anodes 580, 585 may be provided with a fixed current that may differ from the current provided to the remaining anodes. These plating current differences can be provided to compensate for the increased plating that generally occurs at the radial position of the workpiece surface proximate the contacts of the cathode contact assembly 185 (FIG. 8).

[0136] Likewise, the current to the individual anodes 580, 585 can be adjusted to provide a radially uniform deposition of metal during seed layer enhancement in accordance with the present invention, including during seed layer enhancement in an electrolytic alkaline bath.

[0137] The computer simulated effect of a predetermined set of plating current differences on the normalized thickness of the electroplated film as a function of the radial position on the microelectronic workpiece over time is shown in FIG. 18. In this simulation, the seed layer was assumed to be uniform at t_0 . As illustrated, there is a substantial difference in the thickness over the radial position on the microelectronic workpiece during the initial portion of the electroplating process. This is generally characteristic of workpieces having seed layers that are highly resistive, such as those that are formed from a highly resistive material or that are very thin. However, as can be seen from FIG. 18, the differential plating that results from the differential current provided to the anodes 580, 585 forms a substantially uniform plated film by the end of the electroplating process. It will be recognized that the particular currents that are to be provided to anodes 580, 585 depends upon numerous factors including, but not necessarily limited to, the desired thickness and material of the electroplated film, the thickness and material of the initial seed layer, the distances between anodes 580, 585 and the surface of the microelectronic workpiece, electrolyte bath properties, etc.

[0138] Anodes 580, 585 may be consumable, but are suitably inert and formed from platinized titanium or some

other inert conductive material. However, as noted above, inert anodes tend to evolve gases that can impair the uniformity of the plated film. To reduce this problem, as well as to reduce the likelihood of the entry of bubbles into the main processing chamber 505, processing base 37 includes several unique features. With respect to anode 580, a small fluid flow path forms a Venturi outlet 590 between the underside of anode 580 and the relatively lower pressure channel 540 (see FIG. 9). This results in a Venturi effect that causes the electroplating solution proximate the surfaces of anode 580 to be drawn away and, further, provides a suction flow (or recirculation flow) that affects the uniformity of the impinging flow at the central portion of the surface of the microelectronic workpiece.

[0139] The Venturi flow path 590 may be shielded to prevent any large bubbles originating from outside the chamber from rising through region 590. Instead, such bubbles enter the bubble-trapping region of the antechamber 510.

[0140] Similarly, electroplating solution sweeps across the surfaces of anodes 585 in a radial direction toward fluid outlet 572 to remove gas bubbles forming at their surfaces. Further, the radial components of the fluid flow at the surface of the microelectronic workpiece assist in sweeping gas bubbles therefrom.

[0141] There are numerous further processing advantages with respect to the illustrated flow through the reactor chamber. As illustrated, the flow through the nozzles 535 is directed away from the microelectronic workpiece surface and, as such, there are no jets of fluid created to disturb the uniformity of the diffusion layer. Although the diffusion layer may not be perfectly uniform, it will be substantially uniform, and any non-uniformity will be relatively gradual as a result. Further, the effect of any minor non-uniformity may be substantially reduced by rotating the microelectronic workpiece during processing. A further advantage relates to the flow at the bottom of the main chamber 505 that is produced by the Venturi outlet, which influences the flow at the centerline thereof. The centerline flow velocity is otherwise difficult to implement and control. However, the strength of the Venturi flow provides a non-intrusive design variable that may be used to affect this aspect of the flow.

[0142] As is also evident from the foregoing reactor design, the flow that is normal to the microelectronic workpiece has a slightly greater magnitude near the center of the microelectronic workpiece and creates a dome-shaped meniscus whenever the microelectronic workpiece is not present (i.e., before the microelectronic workpiece is lowered into the fluid). The dome-shaped meniscus assists in minimizing bubble entrapment as the microelectronic workpiece or other workpiece is lowered into the processing solution (here, the electroplating solution).

[0143] A still further advantage of the foregoing reactor design is that it assists in preventing bubbles that find their way to the chamber inlet from reaching the microelectronic workpiece. To this end, the flow pattern is such that the solution travels downward just before entering the main chamber. As such, bubbles remain in the antechamber and escape through holes at the top thereof. Further, the upward sloping inlet path (see FIG. 12 and appertaining description) to the antechamber prevents bubbles from entering the main chamber through the Venturi flow path.

[0144] FIGS. 10-12 illustrate a specific construction of a complete processing chamber assembly 610 that has been specifically adapted for electrochemical processing of a semiconductor microelectronic workpiece. More particularly, the illustrated embodiment is specifically adapted for depositing a uniform layer of material on the surface of the workpiece using electroplating.

[0145] As illustrated, the processing base 137 shown in FIG. 8 is comprised of processing chamber assembly 610 along with a corresponding exterior cup 605. Processing chamber assembly 610 is disposed within exterior cup 605 to allow exterior cup 605 to receive spent processing fluid that overflows from the processing chamber assembly 610. A flange 615 extends about the assembly 610 for securement with, for example, the frame of the corresponding tool.

[0146] With particular reference to FIGS. 11 and 12, the flange of the exterior cup 605 is formed to engage or otherwise accept rotor assembly 75 of reactor head 30 (shown in FIG. 8) and allow contact between the microelectronic workpiece 25 and the processing solution, such as electroplating solution, in the main fluid flow chamber 505. The exterior cup 605 also includes a main cylindrical housing 625 into which a drain cup member 627 is disposed. The drain cup member 627 includes an outer surface having channels 629 that, together with the interior wall of main cylindrical housing 625, form one or more helical flow chambers 640 that serve as an outlet for the processing solution. Processing fluid overflowing a weir member 739 at the top of processing cup 35 drains through the helical flow chambers 640 and exits an outlet (not illustrated) where it is either disposed of or replenished and re-circulated. This configuration is particularly suitable for systems that include fluid re-circulation since it assists in reducing the mixing of gases with the processing solution thereby further reducing the likelihood that gas bubbles will interfere with the uniformity of the diffusion layer at the workpiece surface.

[0147] In the illustrated embodiment, antechamber 510 is defined by the walls of a plurality of separate components. More particularly, antechamber 510 is defined by the interior walls of drain cup member 627, an anode support member 697, the interior and exterior walls of a mid-chamber member 690, and the exterior walls of flow diffuser 525.

[0148] FIGS. 10B and 11 illustrate the manner in which the foregoing components are brought together to form the reactor. To this end, the mid-chamber member 690 is disposed interior of the drain cup member 627 and includes a plurality of leg supports 692 that sit upon a bottom wall thereof. The anode support member 697 includes an outer wall that engages a flange that is disposed about the interior of drain cup member 627. The anode support member 697 also includes a channel 705 that sits upon and engages an upper portion of flow diffuser 525, and a further channel 710 that sits upon and engages an upper rim of nozzle assembly 530. Mid-chamber member 690 also includes a centrally disposed receptacle 715 that is dimensioned to accept the lower portion of nozzle assembly 530. Likewise, an annular channel 725 is disposed radially exterior of the annular receptacle 715 to engage a lower portion of flow diffuser 525.

[0149] In the illustrated embodiment, the flow diffuser 525 is formed as a single piece and includes a plurality of vertically oriented slots 670. Similarly, the nozzle assembly

530 is formed as a single piece and includes a plurality of horizontally oriented slots that constitute the nozzles 535.

[0150] The anode support member 697 includes a plurality of annular grooves that are dimensioned to accept corresponding annular anode assemblies 785. Each anode assembly 785 includes an anode 585 (suitably formed from platinized titanium or another inert metal) and a conduit 730 extending from a central portion of the anode 585 through which a metal conductor may be disposed to electrically connect the anode 585 of each assembly 785 to an external source of electrical power. Conduit 730 is shown to extend entirely through the processing chamber assembly 610 and is secured at the bottom thereof by a respective fitting 733. In this manner, anode assemblies 785 effectively urge the anode support member 697 downward to clamp the flow diffuser 525, nozzle assembly 530, mid-chamber member 690, and drain cup member 627 against the bottom portion 737 of the exterior cup 605. This allows for easy assembly and disassembly of the processing chamber 610. However, it will be recognized that other means may be used to secure the chamber elements together as well as to conduct the necessary electrical power to the anodes.

[0151] The illustrated embodiment also includes a weir member 739 that detachably snaps or otherwise easily secures to the upper exterior portion of anode support member 697. As shown, weir member 739 includes a rim 742 that forms a weir over which the processing solution flows into the helical flow chamber 640. Weir member 739 also includes a transversely extending flange 744 that extends radially inward and forms an electric field shield over all or portions of one or more of the anodes 585. Since the weir member 739 may be easily removed and replaced, the processing chamber assembly 610 may be readily reconfigured and adapted to provide different electric field shapes. Such differing electrical field shapes are particularly useful in those instances in which the reactor must be configured to process more than one size or shape of a workpiece. Additionally, this allows the reactor to be configured to accommodate workpieces that are of the same size, but have different plating area requirements.

[0152] The anode support member 697, with the anodes 585 in place, forms the contoured sidewall 560 and slanted sidewall 565 that is illustrated in FIG. 9. As noted above, the lower region of anode support member 697 is contoured to define the upper interior wall of antechamber 510 and suitably includes one or more gas outlets 665 that are disposed therethrough to allow gas bubbles to exit from the antechamber 510 to the exterior environment.

[0153] With particular reference to FIG. 12, fluid inlet 515 is defined by an inlet fluid guide, shown generally at 810, that is secured to the floor of mid-chamber member 690 by one or more fasteners 815. Inlet fluid guide 810 includes a plurality of open channels 817 that guide fluid received at fluid inlet 515 to an area beneath mid-chamber member 690. Channels 817 of the illustrated embodiment are defined by upwardly angled walls 819. Processing fluid exiting channels 817 flows therefrom to one or more further channels 821 that are likewise defined by walls that angle upward.

[0154] Central anode 580 includes an electrical connection rod 581 that proceeds to the exterior of the processing chamber assembly 610 through central apertures formed in nozzle assembly 530, mid-chamber member 690 and inlet

fluid guide 810. The small Venturi flow path regions shown at 590 in FIG. 9 are formed in FIG. 12 by vertical channels 823 that proceed through drain cup member 690 and the bottom wall of nozzle member 530. As illustrated, the fluid inlet guide 810 and, specifically, the upwardly angled walls 819 extend radially beyond the shielded vertical channels 823 so that any bubbles entering the inlet proceed through the upward channels 821 rather than through the vertical channels 823.

[0155] FIGS. 13-16 illustrate a further embodiment of an improved reactor chamber. The embodiment illustrated in these figures retains the advantageous electric field and flow characteristics of the foregoing reactor construction while concurrently being useful for situations in which anode/electrode isolation is desirable. Such situations include, but are not limited to, the following:

- [0156] 1. instances in which the electrochemical electroplating solution must pass over an electrode, such as an anode, at a high flow rate to be optimally effective;
- [0157] 2. instances in which one or more gases evolving from the electrochemical reactions at the anode surface must be removed in order to insure uniform electrochemical processing; and
- [0158] 3. instances in which consumable electrodes are used.

[0159] With reference to FIGS. 13 and 14, the reactor includes an electrochemical electroplating solution flow path into the innermost portion of the processing chamber that is very similar to the flow path of the embodiment illustrated in FIG. 9 and as implemented in the embodiment of the reactor chamber shown in FIGS. 10A through 12. As such, components that have similar functions are not further identified here for the sake of simplicity. Rather, only those portions of the reactor that significantly differ from the foregoing embodiment are identified and described below.

[0160] A significant distinction between the embodiments exists, however, in connection with the anode electrodes and the appertaining structures and fluid flow paths. More particularly, the reactor based 137 includes a plurality of ring-shaped anodes 1015, 1020, 1025 and 1030 that are concentrically disposed with respect to one another in respective anode chamber housings 1017, 1022, 1027 and 1032. As shown, each anode 1015, 1020, 1025 and 1030 has a vertically oriented surface area that is greater than the surface area of the corresponding anodes shown in the foregoing embodiments. Four such anodes are employed in the disclosed embodiment, but a larger or smaller number of anodes may be used depending upon the electrochemical processing parameters and results that are desired. Each anode 1015, 1020, 1025 and 1030 is supported in the respective anode chamber housing 1017, 1022, 1027 and 1032 by at least one corresponding support/conductive member 1050 that extends through the bottom of the processing base 137 and terminates at an electrical connector 1055 for connection to an electrical power source.

[0161] In accordance with the disclosed embodiment, fluid flow to and through the three outer most chamber housings 1022, 1027 and 1032 is provided from an inlet 1060 that is separate from inlet 515, which supplies the fluid flow through an innermost chamber housing 1017. As shown,

fluid inlet 1060 provides electroplating solution to a manifold 1065 having a plurality of slots 1070 disposed in its exterior wall. Slots 1070 are in fluid communication with a plenum 1075 that includes a plurality of openings 1080 through which the electroplating solution respectively enters the three anode chamber housings 1022, 1027 and 1032. Fluid entering the anode chamber housings 1017, 1022, 1027 and 1032 flows over at least one vertical surface and, suitably, both vertical surfaces of the respective anode 1015, 1020, 1025 and 1030.

[0162] Each anode chamber housing 1017, 1022, 1027 and 1032 includes an upper outlet region that opens to a respective cup 1085. Cups 1085, as illustrated, are disposed in the reactor chamber so that they are concentric with one another. Each cup includes an upper rim 1090 that terminates at a predetermined height with respect to the other rims, with the rim of each cup terminating at a height that is vertically below the immediately adjacent outer concentric cup. Each of the three innermost cups further includes a substantially vertical exterior wall 1095 and a slanted interior wall 1200. This wall construction creates a flow region 1205 in the interstitial region between concentrically disposed cups (excepting the innermost cup that has a contoured interior wall that defines the fluid flow region 1205 and then the outer most flow region 1205 associated with the outer most anode) that increases in area as the fluid flows upward toward the surface of the microelectronic workpiece under process. The increase in area effectively reduces the fluid flow velocity along the vertical fluid flow path, with the velocity being greater at a lower portion of the flow region 1205 when compared to the velocity of the fluid flow at the upper portion of the particular flow region.

[0163] The interstitial region between the rims of concentrically adjacent cups effectively defines the size and shape of each of a plurality of virtual anodes, each virtual anode being respectively associated with a corresponding anode disposed in its respective anode chamber housing. The size and shape of each virtual anode that is seen by the microelectronic workpiece under process is generally independent of the size and shape of the corresponding actual anode. As such, consumable anodes that vary in size and shape over time as they are used can be employed for anodes 1015, 1020, 1025 and 1030 without a corresponding change in the overall anode configuration is seen by the microelectronic workpiece under process. Further, given the deceleration experienced by the fluid flow as it proceeds vertically through flow regions 1205, a high fluid flow velocity may be introduced across the vertical surfaces of the anodes 1015, 1020, 1025 and 1030 in the anode chamber housings 1022, 1027 and 1032 while concurrently producing a very uniform fluid flow pattern radially across the surface of the microelectronic workpiece under process. Such a high fluid flow velocity across the vertical surfaces of the anodes 1015, 1020, 1025 and 1030, as noted above, is desirable when using certain electrochemical electroplating solutions, such as electroplating fluids available from Atotech. Further, such high fluid flow velocities may be used to assist in removing some of the gas bubbles that form at the surface of the anodes, particularly inert anodes. To this end, each of the anode chamber housings 1017, 1022, 1027 and 1032 may be provided with one or more gas outlets (not illustrated) at the upper portion thereof to vent such gases.

[0164] Of further note, unlike the foregoing embodiment, element 1210 is a securement that is formed from a dielectric material. The securement 1210 is used to clamp a plurality of the structures forming reactor base 137 together. Although securement 1210 may be formed from a conductive material so that it may function as an anode, the innermost anode seen by the microelectronic workpiece under process is suitably a virtual anode corresponding to the interior most anode 1015.

[0165] FIGS. 15 and 16 illustrate computer simulations of fluid flow velocity contours of a reactor constructed in accordance with the embodiment shown in FIGS. 17 through 19. In this embodiment, all of the anodes of the reactor base may be isolated from a flow of fluid through the anode chamber housings. To this end, FIG. 15 illustrates the fluid flow velocity contours that occur when a flow of electroplating solution is provided through each of the anode chamber housings, while FIG. 16 illustrates the fluid flow velocity contours that occur when there is no flow of electroplating solution provided through the anode chamber housings past the anodes. This latter condition can be accomplished in the reactor of by turning off the flow from the second fluid flow inlet (described below) and may likewise be accomplished in the reactor of FIGS. 13 and 14 by turning of the fluid flow through inlet 1060. Such a condition may be desirable in those instances in which a flow of electroplating solution across the surface of the anodes is found to significantly reduce the organic additive concentration of the solution.

[0166] FIG. 19 illustrates a variation of the reactor embodiment shown in FIG. 14. For the sake of simplicity, only the elements pertinent to the following discussion are provided with reference numerals.

[0167] This further embodiment employs a different structure for providing fluid flow to the anodes 1015, 1020, 1025 and 1030. More particularly, the further embodiment employs an inlet member 2010 that serves as an inlet for the supply and distribution of the processing fluid to the anode chamber housings 1017, 1022, 1027 and 1032.

[0168] With reference to FIGS. 19 and 20, the inlet member 2010 includes a hollow stem 2015 that may be used to provide a flow of electroplating fluid. The hollow stem 2015 terminates at a stepped hub 2020. Stepped hub 2020 includes a plurality of steps 2025 that each include a groove dimensioned to receive and support a corresponding wall of the anode chamber housings. Processing fluid is directed into the anode chamber housings through a plurality of channels 2030 that proceed from a manifold area into the respective anode chamber housing.

[0169] This latter inlet arrangement assists in further electrically isolating anodes 1015, 1020, 1025 and 1030 from one another. Such electrical isolation occurs due to the increased resistance of the electrical flow path between the anodes. The increased resistance is a direct result of the increased length of the fluid flow paths that exist between the anode chamber housings.

[0170] The manner in which the electroplating power is supplied to the microelectronic workpiece at the peripheral edge thereof effects the overall film quality of the deposited metal. Some of the more desirable characteristics of a

contact assembly used to provide such electroplating power include, for example, the following:

[0171] 1. uniform distribution of electroplating power about the periphery of the microelectronic workpiece to maximize the uniformity of the deposited film;

[0172] 2. consistent contact characteristics to insure wafer-to-wafer uniformity;

[0173] 3. minimal intrusion of the contact assembly on the microelectronic workpiece periphery to maximize the available area for device production; and

[0174] 4. minimal plating on the barrier layer about the microelectronic workpiece periphery to inhibit peeling and/or flaking.

[0175] To meet one or more of the foregoing characteristics, reactor assembly 120 suitably employs a contact assembly 185 that provides either a continuous electrical contact or a high number of discrete electrical contacts with the microelectronic workpiece 125. By providing a more continuous contact with the outer peripheral edges of the microelectronic workpiece 125, in this case around the outer circumference of the semiconductor wafer, a more uniform current is supplied to the microelectronic workpiece 125 that promotes more uniform current densities. The more uniform current densities enhance uniformity in the depth of the deposited material.

[0176] Contact assembly 185, in accordance with an embodiment, includes contact members that provide minimal intrusion about the microelectronic workpiece periphery while concurrently providing consistent contact with the seed layer. Contact with the seed layer is enhanced by using a contact member structure that provides a wiping action against the seed layer as the microelectronic workpiece is brought into engagement with the contact assembly. This wiping action assists in removing any oxides at the seed layer surface thereby enhancing the electrical contact between the contact structure and the seed layer. As a result, uniformity of the current densities about the microelectronic workpiece periphery are increased and the resulting film is more uniform. Further, such consistency in the electrical contact facilitates greater consistency in the electroplating process from wafer-to-wafer thereby increasing wafer-to-wafer uniformity.

[0177] Contact assembly 185, as will be set forth in further detail below, also suitably includes one or more structures that provide a barrier, individually or in cooperation with other structures, that separates the contact/contacts, the peripheral edge portions and backside of the microelectronic workpiece 125 from the plating solution. This prevents the plating of metal onto the individual contacts and, further, assists in preventing any exposed portions of the barrier layer near the edge of the microelectronic workpiece 125 from being exposed to the electroplating environment. As a result, plating of the barrier layer and the appertaining potential for contamination due to flaking of any loosely adhered electroplated material is substantially limited. Exemplary contact assemblies suitable for use in the present system are illustrated in U.S. Ser. No. 09/113,723, filed Jul. 10, 1998, which is hereby incorporated by reference.

[0178] One or more of the foregoing reactor assemblies may be readily integrated in a processing tool that is capable

of executing a plurality of processes on a workpiece, such as a semiconductor microelectronic workpiece. One such processing tool is the LT-210TM electroplating apparatus available from Semitool, Inc., of Kalispell, Mont. FIGS. 21 and 22 illustrate such integration.

[0179] The system of FIG. 21 includes a plurality of processing stations 1610. Suitably, these processing stations include one or more rinsing/drying stations and one or more electroplating stations (including one or more electroplating reactors such as the one above), although further immersion-chemical processing stations constructed in accordance with the of the present invention may also be employed. The system also suitably includes a thermal processing station, such as at 1615, that includes at least one thermal reactor that is adapted for rapid thermal processing (RTP).

[0180] The workpieces are transferred between the processing stations 1610 and the RTP station 1615 using one or more robotic transfer mechanisms 1620 that are disposed for linear movement along a central track 1625. One or more of the stations 1610 may also incorporate structures that are adapted for executing an in-situ rinse. Suitably, all of the processing stations as well as the robotic transfer mechanisms are disposed in a cabinet that is provided with filtered air at a positive pressure to thereby limit airborne contaminants that may reduce the effectiveness of the microelectronic workpiece processing.

[0181] FIG. 22 illustrates a further embodiment of a processing tool in which an RTP station 1635, located in portion 1630, that includes at least one thermal reactor, may be integrated in a tool set. Unlike the embodiment of FIG. 21, in this embodiment, at least one thermal reactor is serviced by a dedicated robotic mechanism 1640. The dedicated robotic mechanism 1640 accepts workpieces that are transferred to it by the robotic transfer mechanisms 1620. Transfer may take place through an intermediate staging door/area 1645. As such, it becomes possible to hygienically separate the RTP portion 1630 of the processing tool from other portions of the tool. Additionally, using such a construction, the illustrated annealing station may be implemented as a separate module that is attached to upgrade an existing tool set. It will be recognized that other types of processing stations may be located in portion 1630 in addition to or instead of RTP station 1635.

[0182] D. Selective Electrode Control

[0183] The selective control and adjustment of the anodes for uniform electrodeposition, such as during electrochemical deposition of metallization structures or seed layer enhancement, will now be further described. FIG. 23 shows a schematic representation of the reactor assembly 120 illustrated in FIG. 8. Thus, as previously described, the reactor includes a reactor head 130 and a reactor base 137.

[0184] As previously described with reference to FIG. 9, the reactor head 130 includes a stationary assembly and a rotor assembly that carries the workpiece 125 and suitably positions it process-side down. The rotor assembly rotates or spins the workpiece 125 while joining its electrically conductive surface. The reactor head 130 thus includes one or more cathode contacts, shown generally at 185, that electrically contact the lower surface of the workpiece 125.

[0185] The reactor base 137 includes an outer overflow container 1710 and an interior processing container 1712. A

flow of electroplating fluid is provided to the processing container 1712 through the inlet 1714. The electroplating fluid fills the interior of processing container 1712 and overflows a weir 1716 formed at the top of processing container 1712. The fluid overflowing weir 1716 then enters overflow container 1710, and exits the reactor 120 through an outlet 1718. Outlet 1718 may be directed to a recirculation system, chemical refurbishment system, or disposal system.

[0186] An electrode assembly, shown generally at 1750, is disposed in the processing container 1712 in contact with the electrochemical processing fluid (here, the electroplating fluid). Electrode assembly 1750 includes a base member 1752 in which a plurality of fluid flow apertures 1754 are disposed. The fluid flow apertures 1754 assist in disbursing the electroplating fluid flow entering inlet 1714 so that the flow of electroplating fluid at the surface of microelectronic workpiece 125 is less localized and radially more uniform. Electrode assembly 1750 also includes an electrode array, shown generally at 1756, that comprises a plurality of individual electrodes 1758 that are supported by base member 1752. Electrode array 1756 may take on any number of physical configurations. The particular physical configuration that is utilized in a given reactor is principally dependent on the particular type and shape of microelectronic workpiece 125 that is to be processed. In the illustrated embodiment, microelectronic workpiece 125 is in the form of a disk-shaped semiconductor wafer. Accordingly, the present inventors have found that the individual electrodes 1758 may be formed as rings of different diameters and that they may be arranged concentrically in alignment with the center of microelectronic workpiece 125. It will be recognized, however, that other electrode array configurations may also be employed without departing from the scope of the present invention.

[0187] When reactor 120 is used to electroplate at least one surface of microelectronic workpiece 125, the surface of the workpiece 125 that is electroplated functions as a cathode in the electrochemical reaction while electrode array 1756 functions as an anode. To this end, the surface of workpiece 125 that is to be electroplated is connected to a negative potential terminal of a power supply 1760 through contacts 185 and the individual electrodes 1758 of electrode array 1756 are connected to positive potential terminals of supply 1760. And the illustrated embodiment, each of the individual electrodes 1758 is connected to a discrete terminal of supply 1760 so that supply 1760 may individually alter one or more electrical parameters, such as the current flow, associated with each of the individual electrodes 1758. As such, each of the individual electrodes 1758 of FIG. 23 is an individually controllable electrode. It will be recognized, however, that one or more of the individual electrodes 1758 of electrode array 1756 may be connected to a common node/terminal of power supply 1760. In such instances, power supply 1760 will alter the one or more electrical parameters of the commonly connected electrodes 1758 concurrently, as opposed to individually, thereby effectively making the commonly connected electrodes 1758 a single, individually controllable electrode. As such, individually controllable electrodes can be formed from physically distinct electrodes that are connected to discrete terminals of power supply 1760 as well as from physically distinct electrodes that are commonly connected to a single discrete

terminal of power supply 1760. Electrode array 1756 suitably comprises at least two individually controllable electrodes.

[0188] Electrode array 1756 and power supply 1760 facilitate localized control of the electrical parameters used to electrochemically process the microelectronic workpiece 125. This localized control of the electrical parameters can be used to provide greater uniformity of the electrochemical processing across the surface of the microelectronic workpiece when compared to a single electrode system. However, determining the electrical parameters for each of the electrodes 1758 in array 1756 to achieve the desired process uniformity can be problematic. Accordingly, the present inventors have developed a method and apparatus that simplifies and substantially automates the determination of the electrical parameters associated with each of the individually controllable electrodes. In accordance with this approach, a plurality of sensitivity values are determined, either experimentally or through numerical simulation, and subsequently used to adjust the electrical parameters associated with each of the individually controllable electrodes. The sensitivity values may be placed in a table or may be in the form of a Jacobian matrix. This table/matrix holds information corresponding to process parameter changes (i.e., thickness of the electroplated film) at various points on the workpiece 125 due to electrical parameter perturbations (i.e., electrical current changes) to each of the individually controllable electrodes. This table/matrix is derived from data from a baseline workpiece plus data from separate runs with a perturbation of a controllable electrical parameter to each of the individually controllable.

[0189] Once the values for the sensitivity table/matrix have been determined, the values may be stored in and used by control system 1765 to control one or more of the electrical parameters that power supply 1760 uses in connection with each of the individually controllable electrodes 1758. FIG. 24 is an exemplary flow diagram illustrating one manner in which the sensitivity table/matrix may be used to calculate an electrical parameter (i.e., current) for each of the individually controllable electrodes 1758 that may be used to meet a target process parameter (i.e., target thickness of the electroplated film).

[0190] In the exemplary process of FIG. 24, control system 1765 utilizes two sets of input parameters along with the sensitivity table/matrix to calculate the required electrical parameters. A first set of input parameters corresponds to the data derived from a test run of the process while using a known, predetermined set of electrical parameters. This first set of input parameters can be derived by first executing a test run on a test workpiece using the predetermined electrical parameter set, as shown at step 1770. For example, a test run can be performed by subjecting a microelectronic workpiece 125 to an electroplating process in which the current provided to each of the individually controllable electrodes 1758 is fixed at a predetermined magnitude for a given period of time.

[0191] After the test run is complete, the physical characteristics (i.e., thickness of the electroplated film) of the test workpiece are measured, as at step 1772, and compared against a second set of input parameters at step 1774. In the illustrated embodiment of the method, the second set of input parameters corresponds to the target physical charac-

teristics of the microelectronic workpiece that are to be ultimately achieved by the process (i.e., the thickness of the electroplated film). Notably, the target physical characteristics can either be uniform over the surface of the microelectronic workpiece 125 or vary over the surface. For example, in the illustrated embodiment, the thickness of an electroplated film on the surface of the microelectronic workpiece 125 can be used as the target physical characteristic, and the user may expressly specify the target thicknesses at various radial distances from the center of the workpiece.

[0192] The first and second set of input parameters are used at step 1774 to generate a set of process error values. To ensure the integrity of the data obtained during the test run, the process error values may be checked at step 1776 to make sure that the values fall within a predetermined range, tolerance, etc. If the process error values do not pass this test, a further test run on a further test workpiece may be executed using a different predetermined electrical parameter set, as at step 1778, and the method begins again. If the process error values meet the test at step 1776, the control system 1765 derives a new electrical parameter set based on calculations including the set of process error values and the values of the sensitivity table/matrix, as at step 1780. Once the new electrical parameter set is derived, the control system 1765 directs power supply 1760 to use the derived electrical parameters in subsequent processing of further microelectronic workpieces to achieve the desired target physical characteristics, as at step 1782.

[0193] With reference again to FIG. 23, the exemplary system illustrates two potential manners in which the first and second set of input parameters may be provided to the control system 1765: a user interface 1784 and a metrics tool 1786. User interface 1784 may be comprised of, for example, a keyboard, a touch-sensitive screen, a voice recognition system, etc. Metrics tool 1786 may be an automated tool that is used to measure the physical characteristics of the test workpiece after the test run. When both a user interface 1784 and a metrics tool 1786 are employed, the user interface 1784 may be used to input the target physical characteristics that are to be achieved by the process while metrics tool 1786 may be used to directly communicate the measured physical characteristics of the test workpiece to the control system 1765. In the absence of a metrics tool that can communicate with control system 1765, the measured physical characteristics of the test workpiece can be provided to control system 1765 through user interface 1784. It will be recognized that other data communications devices may be used to provide the first and second set of input parameters to control system 1765, the foregoing being merely exemplary.

[0194] The foregoing method and apparatus can further be understood with reference to a specific embodiment in which the electrochemical process is electroplating, the thickness of the electroplated film is the target physical parameter, and the current provided to each of the individually controlled electrodes 1758 is the electrical parameter that is to be controlled to achieve the target film thickness. In accordance with this specific embodiment, a Jacobian sensitivity matrix is first derived from experimental or numerically simulated data. FIG. 25 is a graph of such data that can be used to derive the Jacobian sensitivity matrix data. As illustrated, FIG. 25 is a graph of the change in electroplated film thickness per change in current-time as a

function of radial position on the microelectronic workpiece 125 for each of the individually controlled anodes A1-A4 of FIG. 23. A first baseline workpiece is electroplated for a predetermined period of time using a predetermined set of current values to individually controlled anodes A1-A4. The thickness of the resulting electroplated film is then measured as a function of the radial position on the workpiece. These data points are then used as baseline measurements that are

[0201] n is an integer representing a particular anode.

[0202] The Jacobian sensitivity matrix, set forth below as Equation (A5), is an index of the Jacobian values computed using Equations (A1)-(A4). These values are also presented as highlighted data points in the graph of FIG. 25. These values correspond to the radial positions on the surface of a semiconductor wafer that are typically chosen for measurement.

$$J = \begin{bmatrix} 0.192982456 & 0.071570577 & 0.030913978 & 0.017811705 \\ 0.148448043 & 0.084824387 & 0.039650538 & 0.022264631 \\ 0.066126856 & 0.087475149 & 0.076612903 & 0.047073791 \\ 0.037112011 & 0.057654076 & 0.090725806 & 0.092239186 \\ 0.029689609 & 0.045725646 & 0.073924731 & 0.138040712 \end{bmatrix} \quad \text{Equation (A5)}$$

compared to the data acquired as the current to each of the anodes A1-A4 is perturbed. Line 1790 is a plot of the data points associated with a perturbation in the current provided by power supply 1760 to anode A1 with the current to the remaining anodes A2-A4 held at their constant predetermined values. Line 1792 is a plot of the data points associated with a perturbation in the current provided by power supply 1760 to anode A2 with the current to the remaining anodes A1 and A3-A4 held at their constant predetermined values. Line 1794 is a plot of the data points associated with a perturbation in the current provided by power supply 1760 to anode A3 with the current to the remaining anodes A1-A2 and A4 held at their constant predetermined values. Lastly, line 1796 is a plot of the data points associated with a perturbation in the current provided by power supply 1760 to anode A4 with the current to the remaining anodes A1-A3 held at their constant predetermined values.

[0195] The data for the Jacobian parameters shown in FIG. 3 may be computed using the following equations:

$$J_{mn} = \frac{\partial t_m}{\partial AM_n} \approx \frac{t_m(AM + \epsilon_n) - t_m(AM)}{|\epsilon_n|} \quad \text{Equation (A1)}$$

$$AM = [AM_1 \ AM_2 \ \dots \ AM_n] \quad \text{Equation (A3)}$$

$$t = t(AM) \quad \text{Equation (A2)}$$

$$\epsilon_1 = \begin{bmatrix} \Delta AM_1 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \quad \epsilon_2 = \begin{bmatrix} 0 \\ \Delta AM_2 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \quad \epsilon_m = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ \Delta AM_m \end{bmatrix} \quad \text{Equation (A4)}$$

[0196] where:

[0197] t represents thickness [microns];

[0198] AM represents current [amp-minutes];

[0199] ϵ represents perturbation [amp-minutes];

[0200] m is an integer corresponding to a radial position on the workpiece; and

[0203] Once the values for the Jacobian sensitivity matrix have been derived, they may be stored in control system 1765 for further use.

[0204] Table 1 below sets forth exemplary data corresponding to a test run in which a 200 mm wafer is plated with copper in a multiple anode system using a nominally 2000 Å thick initial copper seed-layer. Identical currents of 1.12 Amps (for 3 minutes) were provided to all four anodes A1-A4. The resulting thickness at five radial locations was then measured and is recorded in the second column of Table 1. The 3 sigma uniformity of the wafer is 9.4% using a 49 point contour map. Target thickness were then provided and are set forth in column 3 of Table 1. The thickness errors (processed errors) between the plated film and the target thickness were then calculated and are provided in the last column of Table 1.

TABLE 1

Data from wafer plated with 1.12 Amps to each anode.			
Radial Location (m)	Measured Thickness (microns)	Target Thickness (microns)	Error (microns)
0	1.1081	1.0291	-0.0790
0.032	1.0778	1.0291	-0.0487
0.063	1.0226	1.0291	-0.0065
0.081	1.0169	1.0291	0.0122
0.098	0.09987	1.0291	0.0304

[0205] The Jacobian sensitivity matrix may then be used along with the thickness error values to provide a further, revised set of anode current values that should yield better film uniformity. The equations summarizing this approach are set forth below:

[0206] $\Delta AM = J^{-1} \Delta t$ (for a square system in which the number of measured radial positions corresponds to the number of individually controlled anodes in the system); and

[0207] $\Delta AM = (J^T J)^{-1} \Delta t$ (for a non-square system in which the number of measured radial positions is different than the number of individually controlled anodes in the system)

[0208] Table 2 shows the foregoing equations as applied to the given data set and the corresponding current changes that have been derived from the equations to meet the target thickness at each radial location (best least square fit). The wafer uniformity obtained with the currents in the last column of Table 2 was 1.7% (compared to 9.4% for the test run wafer). This procedure can be repeated again to try to further improve the uniformity. In this example, the differences between the seed layers were ignored.

TABLE 2

Anode #	Current adjustment		
	Anode Currents for Run#1 (Amps)	Change to Anode Currents (Amps)	Anode Currents for Run#2 (Amps)
1	1.12	-0.21	0.91
2	1.12	0.20	1.32
3	1.12	-0.09	1.03
4	1.12	0.10	1.22

[0209] Once the corrected values for the anode currents have been calculated, control system 1765 of FIG. 23 directs power supply 1760 to provide the corrected current to the respective anode A1-A4 during subsequent processes to meet the target film thickness and uniformity.

[0210] In some instances, it may be desirable to iteratively apply the foregoing equations to arrive at a set of current change values (the values represented in column 3 of Table 2) that add up to zero. This may be desirable when, for example, the processing recipe defined by the user is entered using amp-minute values.

[0211] The Jacobian sensitivity matrix in the foregoing example quantifies the system response to anode current changes about a baseline condition. Ideally, a different matrix may be employed if the processing conditions vary significantly from the baseline. The number of system parameters that may influence the sensitivity values of the sensitivity matrix is quite large. Such system parameters include the seed layer thickness, the electrolyte conductivity, the metal being plated, the film thickness, the plating rate, the contact ring geometry, the wafer position relative to the chamber, and the anode shape/current distribution. Anode shape/current distribution is included for the case of consumable anodes where the anode shape changes over time. Changes to all of these items can change the current density across the wafer for a given set of anode currents and, as a result, can change the response of the system to changes in the anode currents. It is expected, however, that small changes to many of these parameters will not require the calculation of a new sensitivity matrix. Nevertheless, a plurality of sensitivity tables/matrices may be derived for different processing conditions and stored in control system 1765. Which of the sensitivity tables/matrices is to be used by the control system 1765 can be entered manually by a user, or can be set automatically depending on measurements taken by certain sensors or the like (i.e., temperature sensors, chemical analysis units, etc.) that indicate the existence of one or more particular processing conditions.

[0212] The foregoing apparatus and methods may also be used to compensate for differences and non-uniformities of the initial seed layer of the microelectronic workpiece.

Generally stated, a blanket seed layer can affect the uniformity of a plated film in two ways:

[0213] If the seed layer non-uniformity changes, this non-uniformity is added to the final film. For example, if the seed layer is 100 Å thinner at the outer edge than expected, the final film thickness will also be 100 Å thinner at the outer edge.

[0214] If the average seed-layer thickness changes significantly, the resistance of the seed-layer will change resulting in a modified current density distribution across the wafer and altered film uniformity. For example, if the seed layer decreases from 2000 Å to 1000 Å, the final film will not only be thinner (because the initial film is thinner) but it will also be relatively thicker at the outer edge due to the higher resistivity of the 1000 Å seed-layer compared to the 2000 Å seed-layer (assuming an edge contact).

[0215] The foregoing apparatus and methods can be used to compensate for such seed-layer deviations. In the first case above, the changes in seed-layer uniformity may be handled in the same manner that errors between target thickness and measured thickness are handled. A pre-measurement of the wafer quantifies changes in the seed-layer thickness at the various radial measurement locations and these changes (errors) are figured into the current adjustment calculations. Using this approach, excellent uniformity results can be obtained on the new seed layer, even on the first attempt at electroplating.

[0216] In the second case noted above, an update of or selection all of the and other stored sensitivity/Jacobian matrix can be used to account for a significantly different resistance of the seed-layer. A simple method to adjust for the new seed layer thickness is to plate a film onto the new seed layer using the same currents used in plating a film on the previous seed layer. The thickness errors measured from this wafer can be used with a sensitivity matrix appropriate for the new seed-layer to adjust the currents.

[0217] The Jacobian matrix analysis or other methods of determining how to selectively control the electrodes A1-A4 can also be used to carry out the seed layer enhancement as set forth above herein, so as to create a more uniform seed layer across the face of the workpiece prior to subsequent electrodeposition. Independent control of electrodes or banks of electrodes is particularly useful for tuning the reactor to compensate for high resistance in the substream or barrier on which the seed layer is formed, both during seed layer enhancement and subsequent deposition.

[0218] The foregoing apparatus and methods may also be used to compensate for reactor-to-reactor variations in a multiple reactor system, such as the LT-210C™ available from Semitool, Inc., of Kalispell, Mont. In such a system, there is a possibility that the anode currents required to plate a specified film might be different on one reactor when compared to another. Some possible sources for such differences include variations in the wafer position due to tolerances in the lift-rotate mechanism, variations in the current provided to each anode due to power supply manufacturing tolerances, variations in the chamber geometry due to manufacturing tolerances, variations in the plating solution, etc.

[0219] In a single anode system, the reactor-to-reactor variation is typically reduced either by reducing hardware

manufacturing tolerances or by making slight hardware modifications to each reactor to compensate for reactor variations. In a multiple anode reactor constructed in accordance with the teachings of the present invention, reactor-to-reactor variations can be reduced/eliminated by running slightly different current sets in each reactor. As long as the reactor variations do not fundamentally change the system response (i.e. the sensitivity matrix), the self-tuning scheme disclosed herein is expected to find anode currents that meet film thickness targets. Reactor-to-reactor variations can be quantified by comparing differences in the final anode currents for each chamber. These differences can be saved in one or more offset tables in the control system 65 so that the same recipe may be utilized in each reactor. In addition, these offset tables may be used to increase the efficiency of entering new processing recipes into the control system 65. Furthermore, these findings can be used to trouble-shoot reactor set up. For example, if the values in the offset table are over a particular threshold, the deviation may indicate a hardware deficiency that needs to be corrected.

[0220] The anode arrangements described hereinabove, such as that illustrated and described in FIG. 9, are particularly well-suited for enhancing seed layers that are deposited on highly resistive barrier layers or substrates, for plating microelectronic workpieces having highly resistive seed layers as well as for plating highly resistive materials on microelectronic workpieces. Generally stated, the more resistive the seed layer or material that is to be deposited, the more the magnitude of the current at the central anode (or central anodes) should be increased to yield a uniform film.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal thereon on the metal seed layer, comprising:

- (a) repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer within a principal fluid chamber of a reactor to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process, comprising supplying electroplating power to a plurality of concentric anodes disposed at different positions within the principal fluid flow chamber relative to the workpiece; and
- (b) electrolytically depositing a metal on the enhanced seed layer under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

2. The process of claim 1 wherein the additional metal is copper.

3. The process of claim 1 wherein the ultra-thin seed layer is formed on a barrier layer deposited on a surface of the workpiece.

4. The process of claim 1 wherein the first electrochemical deposition step occurs in an alkaline bath.

5. The process of claim 4 wherein the alkaline bath comprises metal ions and an agent effective in complexing the metal ions.

6. The process of claim 1 wherein the ultra-thin metal seed layer that is repaired is formed by physical vapor deposition.

7. The process of claim 1 wherein the ultra-thin metal seed layer that is repaired has a thickness of less than or equal to 500 Angstroms.

8. The process of claim 7 wherein the ultra-thin metal layer that is repaired has a thickness of 100 to 250 Angstroms.

9. The process of claim 1 wherein the complexing agent comprises one or more complexing agents selected from EDTA, ED, and polycarboxylic acid.

10. The process of claim 9 wherein the complexing agent comprises EDTA and the EDTA in the bath has a concentration within the range of 0.03 to 1.0 M.

11. The process of claim 10 wherein the complexing agent comprises ED and wherein the ED in the electrolytic bath has a concentration within the range of 0.03 to 1.0 M.

12. The process of claim 10 wherein the complexing agent comprises citric acid and the citric acid in the bath has a concentration within the range of 0.03 to 1.0 M.

13. The process of claim 1 wherein the step of subjecting the workpiece to a further electrochemical deposition process occurs in an acidic electrolytic solution to complete deposition of the metal to a thickness needed for the formation of the interconnect structure.

14. The process of claim 13, further comprising subjecting the workpiece to a rinsing process after electrochemical deposition in the alkaline bath and prior to the further electrochemical metal deposition process in an acidic electrolytic solution.

15. The process of claim 1, wherein the enhanced seed layer has a thickness at all points on sidewalls of substantially all recessed features distributed within the workpiece that is equal to or greater than 10% of the enhanced seed layer thickness over the exteriorly disposed surface of the workpiece.

16. The process of claim 1, wherein one or more of the plurality of concentric anodes used to repair the ultra-thin metal seed layer is disposed in close proximity to the workpiece.

17. The process of claim 1, wherein the plurality of concentric anodes used for the repair of the ultra-thin metal seed layer are arranged at varying distances from the workpiece from an innermost one of the plurality of concentric anodes to an outermost one of the plurality of concentric anodes.

18. The process of claim 18, wherein the plurality of concentric anodes used for the repair of the ultra-thin metal seed layer are arranged at increasing distances from the workpiece from an innermost one of the plurality of concentric anodes to an outermost one of the plurality of concentric anodes.

19. The process of claim 1, wherein one or more of the plurality of concentric anodes used to repair the ultra-thin metal seed layer is a virtual anode.

20. The process of claim 19, wherein the virtual anode used in the repair of the ultra-thin metal seed layer comprises an anode chamber housing having a processing fluid inlet and a processing fluid outlet, the processing fluid outlet

being disposed in close proximity to the workpiece, and at least one conductive anode element disposed in the anode chamber housing.

21. The process of claim 20, wherein the at least one conductive anode element is formed from an inert material.

22. The process of claim 1, wherein the repair of the ultra-thin metal seed layer is further carried out by providing a plurality of nozzles within the reactor that are disposed to provide a flow of a processing fluid to the principal fluid flow chamber, the plurality of nozzles being arranged and directed to provide vertical and radial fluid flow components that combine to generate a substantially uniform normal flow component oriented radially across a surface of the workpiece on which the ultra-thin metal seed layer is formed.

23. The process of claim 1, wherein the principal fluid chamber in which the repair of the ultra-thin metal seed layer is carried out is defined in an upper portion thereof by an angled wall, the angled wall supporting one or more of the plurality of the concentric anodes.

24. The process of claim 1, wherein the repair of the ultra-thin metal seed layer is carried out in a principal fluid flow chamber that comprises an inlet disposed at a lower portion thereof and that is configured to provide a venturi effect that facilitates recirculation of a chemical processing fluid in a lower portion of the principal fluid flow chamber.

25. The process of claim 1, wherein during the repair of the ultra-thin metal seed layer, at least two of the plurality of anodes are independently connected to an electrical power supply, further comprising independently controlling the supply of electrical power to the at least two of the plurality of anodes.

26. The process of claim 25, wherein the controlling of the supply of power for at least one of the independently controlled anodes is based on one or more user input parameters and a plurality of predetermined sensitivity values associated with the workpiece, the predetermined sensitivity values corresponding to process perturbations resulting from perturbations of an electrical power supply parameter for the at least one independently controlled electrode.

27. The process of claim 26, wherein the electrical power parameter is electrical current.

28. The process of claim 26, wherein the sensitivity values are logically arranged within a controller as one or more Jacobian matrices.

29. The process of claim 26, wherein the at least one user input parameter comprises a thickness of the additional metal to be deposited on the ultra-thin metal seed layer.

30. The product produced by the process of claim 1.

31. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal thereon on the metal seed layer, comprising:

(a) repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer within a principal fluid chamber of a reactor to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process, comprising supplying electro-

plating power to a plurality of electrodes within the principal fluid flow chamber, wherein at least two of the plurality of electrodes are independently connected to an electrical power supply, further comprising independently controlling the supply of electrical power to the at least two electrodes during repair of the ultra-thin metal seed layer; and

(b) electrolytically depositing a metal on the enhanced seed layer under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

32. The process of claim 31 wherein the additional metal is copper.

33. The process of claim 31 wherein the ultra-thin seed layer is formed on a barrier layer deposited on a surface of the workpiece.

34. The process of claim 31 wherein the electrochemical deposition step occurs in an alkaline bath.

35. The process of claim 31 wherein the ultra-thin metal seed layer that is repaired has a thickness of less than or equal to 500 Angstroms.

36. The process of claim 31, wherein the controlling of the supply of power for at least one of the independently controlled electrodes is based on one or more user input parameters and a plurality of predetermined sensitivity values associated with the workpiece, the predetermined sensitivity values corresponding to process perturbations resulting from perturbations of an electrical power supply parameter for the at least one independently controlled electrode.

37. The process of claim 36, wherein the electrical power parameter is electrical current or potential.

38. The process of claim 36, wherein the sensitivity values are logically arranged within a controller as one or more Jacobian matrices.

39. The process of claim 26, wherein the at least one user input parameter comprises a thickness of the additional metal to be deposited on the ultra-thin metal seed layer.

40. The product produced by the process of claim 31.

41. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrochemical deposition of a metal thereon on the metal seed layer, comprising:

(a) subjecting the workpiece to an electrochemical deposition process that is different from the first deposition process, in an alkaline electroplating bath comprising metal ions complexed with a complexing agent such that additional metal is deposited on the ultra-thin copper seed layer to thereby repair the seed layer, resulting in an enhanced seed layer, the second deposition process being carried out by supplying electroplating power to a plurality of concentric anodes disposed at different positions, relative to the workpiece, within a principal fluid flow chamber of a reactor; and

(b) electrolytically depositing a metal on the enhanced seed layer under conditions in which the deposition rate of the electrolytic deposition process is substantially

greater than the deposition rate of the process used to repair the metal seed layer.

42. The process of claim 41 wherein the additional metal is copper.

43. The process of claim 41 wherein the ultra-thin seed layer is formed on a barrier layer deposited on a surface of the workpiece.

44. The process of claim 41 wherein the complexing agent comprises one or more complexing agents selected from EDTA, ED, and polycarboxylic acid.

45. The process of claim 41 wherein the ultra-thin metal seed layer that is repaired has a thickness of less than or equal to 500 Angstroms.

46. The process of claim 41, wherein during the repair of the ultra-thin metal seed layer, at least two of the plurality of anodes are independently connected to an electrical power supply, further comprising independently controlling the supply of electrical power to the at least two of the plurality of anodes.

47. The process of claim 26, wherein the controlling of the supply of power for a given one of the independently controlled electrodes is based on one or more user input parameters and the plurality of predetermined sensitivity values associated with the workpiece, the predetermined sensitivity values corresponding to process perturbations resulting from perturbations of an electrical power supply parameter for the at least one independently controlled electrode.

48. The process of claim 47, wherein the sensitivity values are logically arranged within a controller as one or more Jacobian matrices.

49. The process of claim 47, wherein the at least one user input parameter comprises a thickness of the additional metal to be deposited on the ultra-thin metal seed layer.

50. The product produced by the process of claim 41.

51. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrochemical deposition of a metal thereon on the metal seed layer, comprising:

(a) subjecting the workpiece to an electrochemical deposition process that is different from the first deposition process, in an alkaline electroplating bath comprising metal ions complexed with a complexing agent such that additional metal is deposited on the ultra-thin copper seed layer to thereby repair the seed layer, resulting in an enhanced seed layer, comprising supplying electroplating power to a plurality of electrodes within the principal fluid flow chamber, wherein at least two of the plurality of electrodes are independently connected to an electrical power supply, further comprising independently controlling the supply of electrical power to the at least two electrodes during repair of the ultra-thin metal seed layer; and

(b) electrolytically depositing a metal on the enhanced seed layer under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

52. The process of claim 51 wherein the additional metal is copper.

53. The process of claim 51 wherein the ultra-thin seed layer is formed on a barrier layer deposited on a surface of the workpiece.

54. The process of claim 51 wherein the complexing agent comprises one or more complexing agents selected from EDTA, ED, and polycarboxylic acid.

55. The process of claim 51 wherein the ultra-thin metal seed layer that is repaired has a thickness of less than or equal to 500 Angstroms.

56. The process of claim 51, wherein the controlling of the supply of power for at least one of the independently controlled electrodes is based on one or more user input parameters and a plurality of predetermined sensitivity values associated with the workpiece, the predetermined sensitivity values corresponding to process perturbations resulting from perturbations of an electrical power supply parameter for the at least one independently controlled electrode.

57. The process of claim 56, wherein the electrical power parameter is electrical current.

58. The process of claim 56, wherein the sensitivity values are logically arranged within a controller as one or more Jacobian matrices.

59. The process of claim 56, wherein the at least one user input parameter comprises a thickness of the additional metal to be deposited on the ultra-thin metal seed layer.

60. The product produced by the process of claim 51.

61. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal thereon on the metal seed layer, comprising:

(a) repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer within a principal fluid chamber of a reactor to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process, comprising exposing the workpiece to an electroplating solution within a fluid flow chamber of a reactor, the fluid flow chamber defining a sidewall and a plurality of nozzles disposed in the sidewall and arranged and directed to provide vertical and radial fluid flow components that combine to create a substantially uniform normal flow component radially across a surface of the workpiece on which the ultra-thin metal seed layer is formed; and

(b) electrochemically depositing a metal on the enhanced seed layer under conditions in which the deposition rate of the deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

62. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally

unsuitable for bulk electrochemical deposition of a metal thereon on the metal seed layer, comprising:

- (a) subjecting the workpiece to an electrochemical deposition process that is different from the first deposition process, in an alkaline electroplating bath comprising metal ions complexed with a complexing agent such that additional metal is deposited on the ultra-thin copper seed layer to thereby repair the seed layer, resulting in an enhanced seed layer, comprising exposing the workpiece to an electroplating solution within a fluid flow chamber of a reactor, the fluid flow chamber defining a sidewall and a plurality of nozzles disposed in the sidewall and arranged and directed to provide vertical and radial fluid flow components that combine to create a substantially uniform normal flow component radially across a surface of the workpiece on which the ultra-thin metal seed layer is formed; and

- (b) electrochemically depositing a metal on the enhanced seed layer under conditions in which the deposition rate of the deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer.

63. The process of claim 62, further comprising applying heat to the metallization interconnect structure after the first electrochemical deposition process to further anchor the seed layer to the underlying layer.

64. The process of claim 62, wherein the first electrochemical deposition process involves depositing a metal alloy including an element that will preferentially be deposited at interfaces defined between differing materials.

65. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal thereon on the metal seed layer, comprising:

- (a) repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer within a principal fluid chamber of a reactor to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process; and

- (b) electrolytically depositing a metal on the enhanced seed layer under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer, comprising supplying electroplating power to a plurality of concentric anodes disposed at different positions within the principal fluid flow chamber relative to the workpiece.

66. The process of claim 65, wherein the second deposition process that repairs the seed layer is an electroless plating process.

67. The process of claim 65, wherein the second deposition process that repairs the said layer also comprises supplying electroplating power to a plurality of concentric anodes disposed at different positions within the principal fluid flow chamber relative to the workpiece.

68. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed

layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal thereon on the metal seed layer, comprising:

- (a) repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process; and

- (b) electrolytically depositing a metal on the enhanced seed layer within a principal fluid chamber of a reactor under conditions in which the deposition rate of the electrolytic deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer, comprising supplying electroplating power to a plurality of electrodes within the principal fluid flow chamber, wherein at least two of the plurality of electrodes are independently connected to an electrical power supply, further comprising independently controlling the supply of electrical power to the at least two electrodes during deposition.

69. The process of claim 68, wherein the second deposition process that repairs the seed layer is an electroless plating process.

70. The process of claim 68, wherein the second deposition process that repairs the said layer occurs within a principal fluid chamber of a reactor and also comprises supplying electroplating power to a plurality of electrodes within the principal fluid flow chamber, wherein at least two of the plurality of electrodes are independently connected to an electrical power supply, further comprising independently controlling the supply of electrical power to the at least two electrodes during deposition.

71. A process for applying a metallization interconnect structure to a workpiece on which an ultra-thin metal seed layer has been formed using a first deposition process, the first deposition process anchoring the ultra-thin metal seed layer to an underlying layer, the ultra-thin metal seed layer having physical characteristics that render it generally unsuitable for bulk electrolytic deposition of a metal thereon on the metal seed layer, comprising:

- (a) repairing the ultra-thin metal seed layer by electrochemically depositing additional metal on the ultra-thin metal seed layer to provide an enhanced seed layer using a second deposition process, that is different from the first deposition process; and

- (b) electrochemically depositing a metal on the enhanced seed layer within a principal fluid chamber of a reactor within a principal fluid chamber of a reactor under conditions in which the deposition rate of the deposition process is substantially greater than the deposition rate of the process used to repair the metal seed layer, comprising exposing the workpiece to an electroplating solution within a fluid flow chamber of a reactor, the fluid flow chamber defining a sidewall and a plurality of nozzles disposed in the sidewall and arranged and directed to provide vertical and radial fluid flow components that combine to create a substantially uniform normal flow component radially across a surface of the workpiece on which the ultra-thin metal seed layer is formed.

72. The process of claim 71, wherein the second deposition process that repairs the seed layer is an electroless plating process.

73. The process of claim 71, wherein the second deposition process that repairs the said layer occurs within a principal fluid chamber of a reactor and also comprises exposing the workpiece to an electroplating solution within a fluid flow chamber of a reactor, the fluid flow chamber

defining a sidewall and a plurality of nozzles disposed in the sidewall and arranged and directed to provide vertical and radial fluid flow components that combine to create a substantially uniform normal flow component radially across a surface of the workpiece on which the ultra-thin metal seed layer is formed.

* * * * *



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(54) **PHOTO-ASSISTED ELECTROLYSIS APPARATUS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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Primary Examiner—Donald R. Valentine

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(74) *Attorney, Agent, or Firm*—Fellers, Snider, Blankenship, Bailey & Tippens, P.C.

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(52) **U.S. Cl.** **204/242; 204/290.01**

(58) **Field of Search** **204/242, 290.01**

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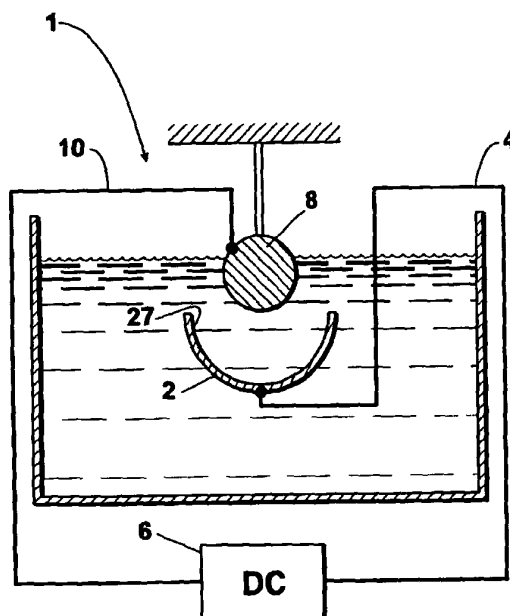
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(57) **ABSTRACT**

An apparatus and method for performing electrolysis on materials such as water, thereby electrically separating the electrolyte into its elemental components. More specifically, according to a preferred aspect of the instant invention, there is provided an apparatus for splitting water into hydrogen and oxygen that uses a specially prepared cathode in conjunction with incident light energy to increase the efficiency of that process. A preferred embodiment of this apparatus uses the photo collector/cathode which comprises a thin layer of metal, preferably nickel, deposited by electroplating or a similar technique onto a conductive surface (e.g., a sheet of copper metal). During the electrolysis process, the cathode is irradiated with light, thereby reducing the amount of electrical energy necessary to separate a given quantity of electrolytic material.

16 Claims, 4 Drawing Sheets



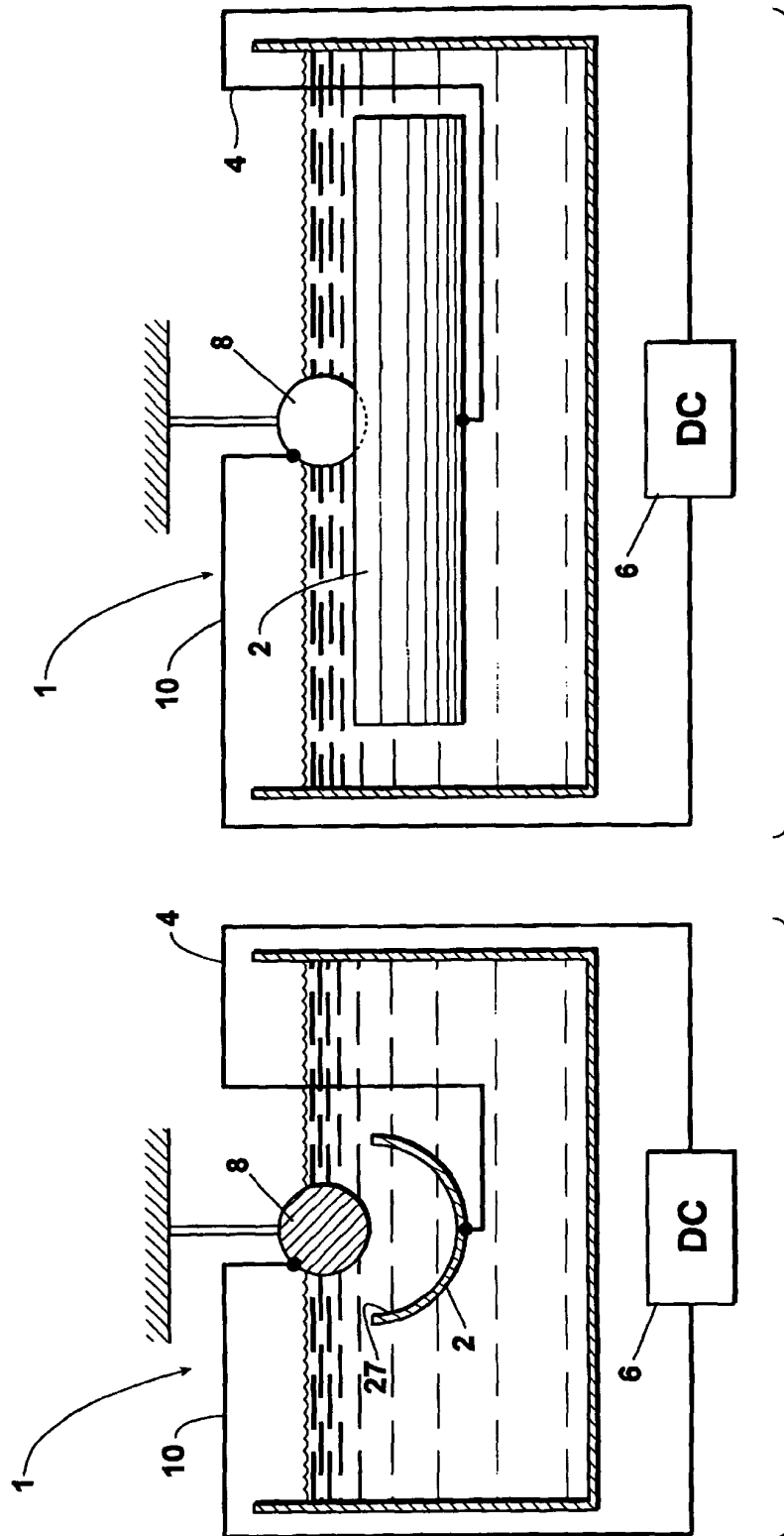
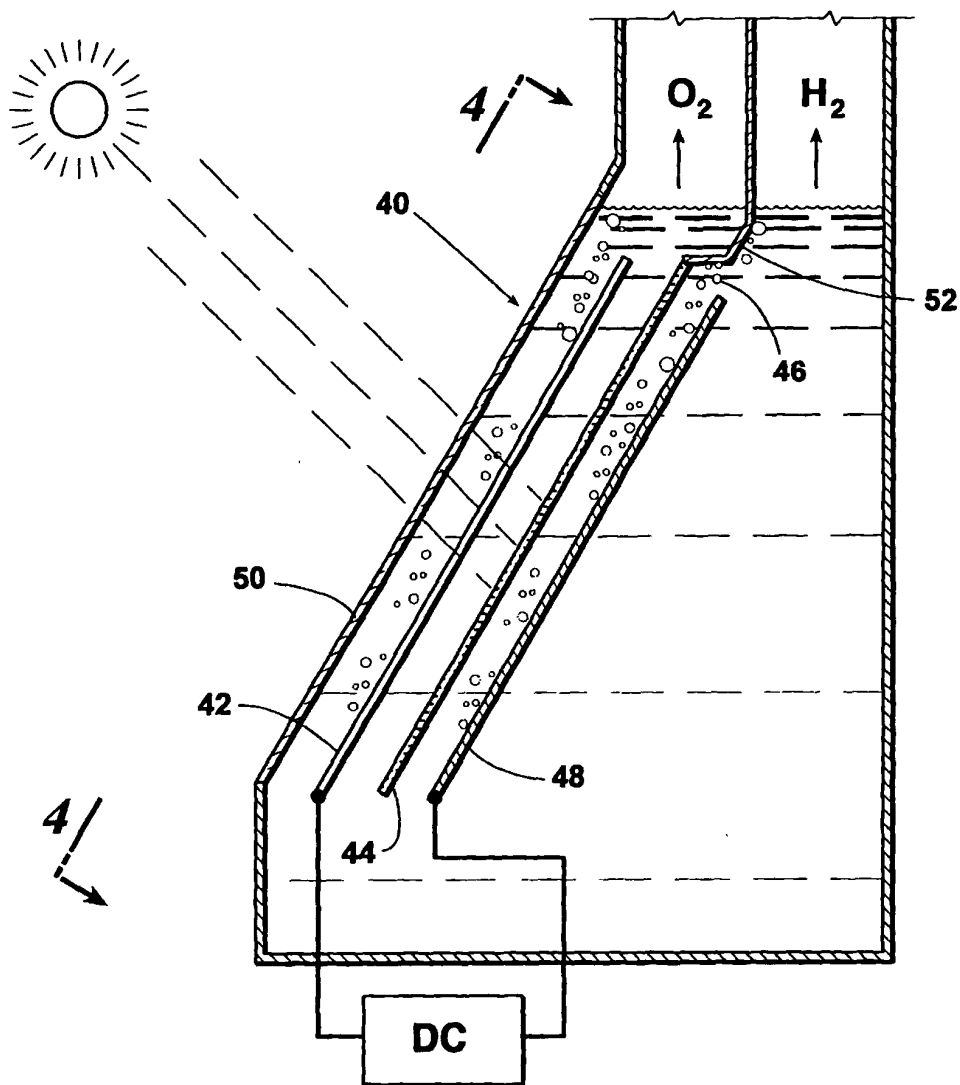
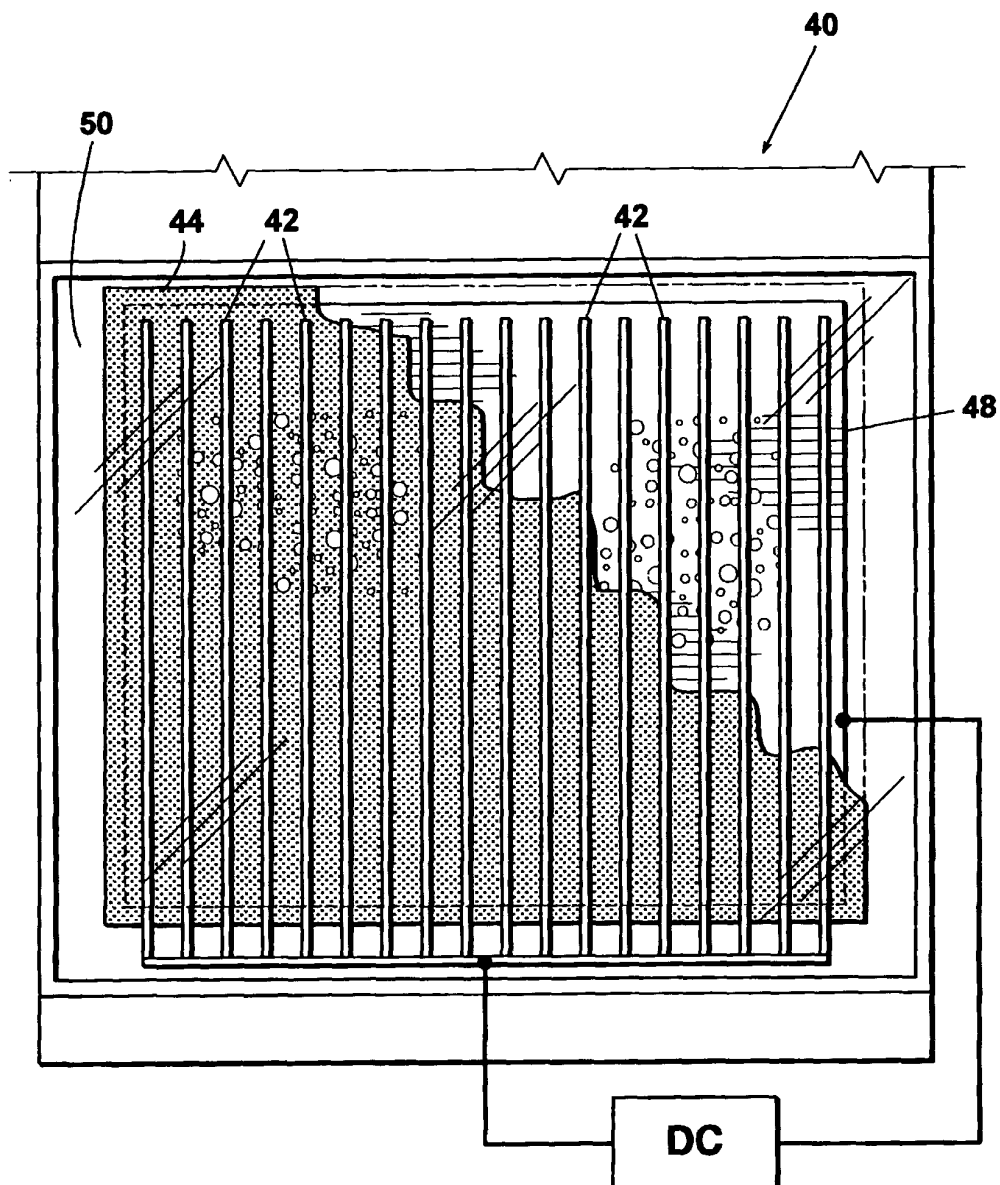


Fig. 2

Fig. 1



*Fig. 4*

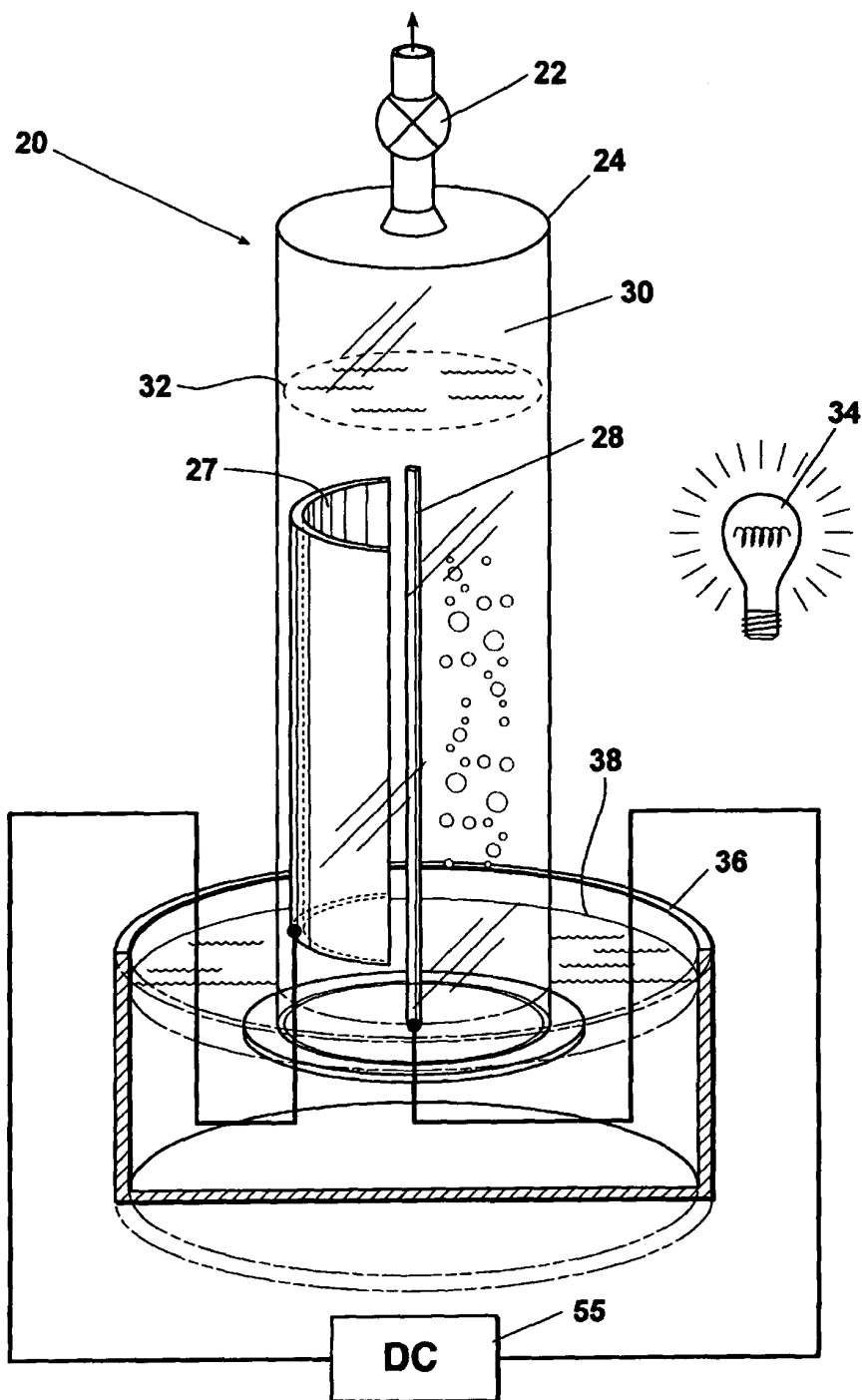
**Fig. 5**

PHOTO-ASSISTED ELECTROLYSIS APPARATUS

This application claims the benefit of Ser. No. 60/179,241, filed Jan. 31, 2000.

TECHNICAL FIELD

The present invention relates generally to the field of electrolysis and, more particularly, to the separation of water into its elemental components via electrical current.

BACKGROUND

Our world has been running on fossil fuels (coal and petroleum) for over two hundred years, and is fast using these fuels up. Since it takes millions of years for these fuels to form, the need for an alternate source of energy is growing more and more urgent. The burning of fossil fuels has also been a major contributor to pollution and a possible cause of global warming.

Wind, water, geothermal and tidal energy sources have all been developed but they are limited to specific places. Fission has been developed as well, but has met sturdy resistance from environmental action groups. Fusion energy has yet to live up to its promise. Solar energy via photovoltaic cells has also been developed but these use less than 15% of the available energy and are not yet cost efficient.

Fuel cells, which produce energy by recombining oxygen and hydrogen to generate electricity, have reached 70 to 80 percent efficiency and, since they produce only water, are non-polluting and do not contribute to the greenhouse effect. Until now, the main source of hydrogen for such systems has been through the electrolysis of water. Because energy is required for the electrolysis process, and because in any system some energy is lost to entropy, this process has been inefficient. Many elaborate methods have been designed to reduce the amount of energy needed to split water. Because these either have not worked, or have been very expensive or inefficient processes, it has not been practical to scale up any of these methods for commercial use.

It has been known for over 100 years that hydrogen and oxygen gas may be generated by the electrolysis of water. Electrolysis utilizes electrical power to create a current between an anode and cathode, thereby breaking water into its constituent components, hydrogen and oxygen. Of course, this process has the potential to be particularly important in view of the concern associated with access to hydrocarbons in politically unstable countries. As is well known to those skilled in the art, hydrogen is a clean, plentiful and readily usable fuel. Needless to say, an efficient and economical method of producing hydrogen from readily available materials such as water could have significant value, especially in countries that have few hydrocarbon deposits. Consequently, there is a growing interest in developing new techniques for the efficient production of molecular hydrogen.

In order to reduce the amount of electrical energy necessary to sunder the hydrogen-oxygen bond in water, solar energy is being explored as an energy source. One approach which has been actively explored involves chemical processes which resemble photosynthesis in order to convert water and air into combustible hydrocarbons. Another approach, which is the approach taken by the instant invention, is to accomplish production of hydrogen gas by using sunlight to effect electrolysis of water. Generally, the emphasis with electrolysis has been to use some type of exotic solid state photoelectric cell to generate current and

release hydrogen and oxygen. To date, the solid state photoelectric approaches have not proven economically successful.

In 1905, Albert Einstein explained the photoelectric effect using the quantum hypothesis. The photoelectric effect involves the ejection of electrons from a metal surface by light in a vacuum tube. Einstein developed the equation for the energy of these electrons in 1906. The equation is:

$$E = h\nu - W$$

This equation means that the energy (E) of the electrons is equal to Plank's constant (h), multiplied by the frequency of the light (ν), minus the work function (W) of the metal.

For the energy of the electrons to equal that needed for the electrolysis of water, the frequency of light must be in the range of high frequency ultraviolet. Thus, solar energy has heretofore had only limited use in producing hydrogen.

Thus, there exists a need for a method and apparatus that provides efficient electrolysis of water into its constituent elements. Accordingly, it should now be recognized, as was recognized by the present inventors, that there exists, and has existed for some time, a very real need for an invention that would address and solve the above-described problems.

Before proceeding to a description of the present invention, however, it should be noted and remembered that the description of the invention which follows, together with the accompanying drawings, should not be construed as limiting the invention to the examples (or preferred embodiments) shown and described. This is so because those skilled in the art to which the invention pertains will be able to devise other forms of this invention within the ambit of the appended claims.

SUMMARY OF THE INVENTION

This instant invention provides an efficient method of performing electrolysis on water, thereby separating it into its elemental components. More specifically, according to a preferred aspect of the instant invention, there is provided an apparatus and method for splitting water into hydrogen and oxygen. The inventive apparatus and method employ a specially prepared cathode in conjunction with incident light energy to increase the efficiency of that process.

According to a first preferred embodiment, there is provided an electrolysis apparatus wherein the cathode serves both as a photon collector and as an electrode for electrolysis. Of particular importance for purposes of the instant invention is the fact that the photon collector/cathode consists of a thin layer of metal, preferably nickel, deposited by electroplating or some similar technique (e.g., vapor deposition) onto a conductive surface (e.g., a sheet of copper metal). The electroplating produces a "blackened" (i.e., black or nearly black or otherwise darkened) surface which appears to be a microcrystalline deposit of metal. This metal "black" serves both to collect and absorb the light and simultaneously acts as a cathodic surface for the electrolysis of water. The material and structure (i.e., the way that the surface metal is deposited) affect the efficiency of the photo-assisted electrolysis and operate to capture energy over a much larger portion of the solar spectrum.

In operation, the anode and specially prepared cathode are preferably immersed in a solution comprising an electrolyte along with the material (e.g., water, acetic acid, or other organic or inorganic compound) that is to be electrolyzed. An electrical potential is then created between the anode and the specially prepared cathode, and the cathode is irradiated with light. Light incident upon the cathode contributes

additional energy to the electrolysis process, thereby reducing the amount of electricity necessary to separate a given quantity of water molecules. Of course, in the preferred embodiment, the incident light will be solar light, although many other light sources might be used. However, solar light sources have the advantage of providing photons to the reaction at no "cost", in contrast to artificial light sources which must be supplied with power, thereby reducing the overall efficiency of the process.

Although light has previously been used to assist in the electrolysis process, such prior usage has occurred within much more complex systems of semiconductors and/or metal ions complexed in organic compounds. Thus, the principle advantage of the instant apparatus and method is that the inventive system operates simply and efficiently to reduce the electrical energy required for electrolysis.

Since much less energy is needed to produce hydrogen using the inventive system, fuels cells can now be run on hydrogen gas (H_2) that is produced much efficiently and cost effectively, thus providing commercial viability. In addition, the inventive method of producing hydrogen gas does not threaten the environment as do fossil and nuclear energy sources.

The inventive system can be employed at any level or scale, from individual cell phones to power plants. Because the process uses inexpensive, readily available materials, it could be used in third world countries, as well as in the earth's most technologically advanced countries. Furthermore, because energy and water are the only products of this process, the problem of pollution has been eliminated.

In addition to hydrogen production, the inventive apparatus and method can also be used in other electrochemical processes. For example, certain organic acids have been shown to decarbonylate and break down under certain electrolysis conditions to methane, ethane and carbon dioxide. This invention can be used to remove or reduce such acids in waste streams through solar assisted electrolysis. A number of similar electrochemical reactions where this invention could be used are known in both organic and inorganic chemistry.

The foregoing has outlined in broad terms the more important features of the invention disclosed herein so that the detailed description that follows may be more clearly understood, and so that the contribution of the instant inventors to the art may be better appreciated. The instant invention is not to be limited in its application to the details of the construction and to the arrangements of the components set forth in the following description or illustrated in the drawings. Rather, the invention is capable of other embodiments and of being practiced and carried out in various other ways not specifically enumerated herein. Finally, it should be understood that the phraseology and terminology employed herein are for the purpose of description and should not be regarded as limiting, unless the specification specifically so limits the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates an end-view of a preferred electroplating apparatus.

FIG. 2 illustrates a side-view of a the electroplating apparatus of FIG. 1.

FIG. 3 provides a side-view of inventive apparatus 40.

FIG. 4 provides a front view of inventive apparatus 40.

FIG. 5 provides a schematic diagram of an embodiment 20 of the inventive electrolysis apparatus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It should be noted at the outset, that within certain broad, general guidelines, the specific details of the geometry and construction of the inventive photo-assisted electrolysis cell are not critical. Indeed, it is well within the ability of one of ordinary skill in the art to construct many different variations of the preferred embodiments given herein. For example, modifications may be made to enhance separation and collection of hydrogen gas and oxygen gas, reduce over-voltage requirements, enhance light collection capabilities, change the ionic composition of the electrolytic solution, etc., without altering the fundamental nature of the invention.

An example of an electroplating bath 1 of a type preferred for use in the present invention is depicted in FIGS. 1 and 2. In the electroplating apparatus 1, 2 is a cathode which is being blacked for use in the inventive electrolysis processes. In this example, the base component of cathode 2 is preferably a half cylinder of conductive metal (e.g., copper metal foil) 2 soldered to a wire 4 connecting it to the DC power supply 6. Element 8 is the electroplating anode (in this particular example a nickel coin, i.e., a disk of nickel-containing metal). Anode 8 is preferably moved back and forth over the inner surface of the cathode to deliver a roughly equivalent (i.e., even) layer of the electroplating metal to all parts of the inner surface of the cathode. Container 1 is an electroplating bath containing a solution of a salt of the metal to be deposited on the surface of the cathode. In this example, the salt would preferably be $NiSO_4$.

In this embodiment of the inventive system, cathode 2 is preferably a flexible sheet of metal (e.g., thin, copper metal) formed into a half cylinder. The radius of this partial cylinder is not critical within broad practical limits. The half cylinder 2 is preferably attached to an insulated, conductive wire 4 by, for example, soldering, and then cleaned to remove surface contamination. The half cylinder 2 is then preferably placed in electroplating bath 1 (e.g., a solution of nickel (II) sulfate dissolved in water) and connected to electrical power source 6 so that it operates as the cathode in the electroplating system 1. Anode 8 is also connected to power source 6, by means of insulated wire 10, to begin electro-deposition of a layer of conductive metal (e.g., nickel) onto the concave inside surface 27 of the half cylinder 2.

As will be understood by those skilled in the art, other physical and chemical approaches to depositing the active surface on cathode 2 are certainly possible and have been specifically contemplated by the instant inventors. The resulting cathode surface should be dark in appearance (rather than having a shiny metallic surface) due to its coating by the reduced metal. As described by some chemists and as used herein and in the claims, this sort of dark surface is referred to as a "black". Although not essential to the invention, it is our belief that this black is a micro-crystalline deposit of the metal in question. The "black" layer will preferably be essentially free of any semiconductor materials and most preferably will consist of conductive metal in elemental form. That being said, it should be noted that the instant invention will operate, albeit not as efficiently, if the "blackened" surface is shiny.

In addition to copper, examples of other materials suitable for forming the underlying base of cathode 2 include: nickel, lead, tin, chromium, graphite or graphitic carbon, gold, silver, chromium, platinum, palladium, and alloys thereof. The base could be even formed of a plastic or other

non-conductive material onto which a conductive surface is applied, for example, by sputtering, painting, or other processes. The base will preferably be essentially free of any semiconductive materials and will most preferably consist essentially of conductive metal in elemental form, the most important property of the base being that it is conductive on the surface that is to form the cathode and sufficiently solid to support the coating(s). Further, it is possible in some cases for the base to also function as the blackening material, e.g., when the base is graphite or graphite carbon.

As will also be apparent to those skilled in the art, electroplating (blackening) metals other than nickel can alternatively be employed in the present invention. By using platinum salts and a platinum anode, for example, a thin surface layer of "platinum black" can be obtained. Examples of other suitable blackening materials include: palladium, copper, silver, gold, zinc, cadmium, thallium, indium, gallium, lead, tin, bismuth, antimony, arsenic, tellurium, selenium, iridium, rhodium, cobalt, iron, ruthenium, osmium, rhenium, manganese, tungsten, molybdenum, chromium, tantalum, niobium, vanadium, titanium, zirconium, lanthanum, ytterbium, scandium, strontium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and lutetium. Examples of additional suitable materials include mixtures, alloys, mercury amalgams, and combinations of the foregoing and similar metals, or combinations of these elements with other elements, where the above elements constitute the major (by weight) components.

The thickness of the "black" deposit is not critical so long as it is thick enough to coat the surface of the cathode and provide a high surface area for hydrogen generation and be dark enough to absorb light efficiently. Nickel, platinum, and palladium are good choices for electroplating as they are known to interact with hydrogen at an atomic level and are used for hydrogenations in organic chemistry. Cobalt is also particularly well suited for use in the inventive apparatus as the cathode plating/blackening metal.

The instant inventors have determined that, if the coating is too thick, it may potentially interfere with the electrical conductivity of the cathode. Thus, for purposes of the overall efficiency of the instant invention, the preferred electrode deposit thickness will be under 1 mm thick, preferably less than 0.1 mm, and in some cases can be as little as only a few atoms thick. If the coating is too thick, the conductivity may suffer. If too thin, light absorption may suffer.

After a suitable amount of metal is deposited on the cathode 2, it is preferably removed from the plating bath, rinsed with water and is ready to be placed in the electrolysis cell.

An embodiment 20 of the inventive electrolysis apparatus is depicted in FIG. 5. Inventive apparatus 20 comprises: an upper valve 22; a barrel 24 (e.g., a barrel of a glass syringe); a cathode preferably prepared as discussed hereinabove and most preferably comprising copper foil with nickel metal electroplated on inside surface 27 thereof; an anode 28 (e.g., a nickel-chromium wire); an upper gas collection space 30 in barrel 24 (wherein both H₂ and O₂ accumulate); a level 32 of electrolyte solution in barrel 24; a light source 34; a base container 36 (e.g., a beaker); and a level 38 of electrolyte solution in base container 36. Inside surface 27 of cathode preferably faces anode 28 and light source 34.

In embodiment 20 of the inventive apparatus, the anode 28 is preferably a conductive wire composed of nickel-chromium alloy (e.g., nichrome). However, all that is nec-

essary is that the anode be a good conductor of electricity and resistant to the corrosive conditions of the anode region of the cell. Examples of other suitable anode materials include: platinum, gold, titanium, nickel, graphite or graphite carbon, and alloys thereof. The anode will preferably be essentially free of any semiconductor materials.

Although many other arrangements are possible, the anode wire 28 is preferably placed adjacent the center of half cylinder cathode along the longitudinal axis thereof so that all points on the inside surface 27 of the cathode 2 are approximately equidistant from the anode 28. The half cylinder cathode 2 is preferably co-axial with the cylinder of barrel 24 and the anode 28 preferably extends along the center of the barrel at least as far as the cathode cylinder 2 extends. Cathode 2 and anode 28 can be kept in place and alignment, for example, by placing a cork or other inert structure in at the bottom of the barrel 24 which will hold the electrodes in place yet allow free movement of water/electrolyte into and out of the bottom of the syringe.

To prepare inventive electrolysis apparatus 20 for operation, valve 22 is opened and the barrel 24 is lowered into the electrolyte solution so that the solution 38 fills the bottom portion of the barrel up to the level in the surrounding container 36. Alternatively, and as further examples may be used to enable outside air to push the electrolyte liquid/solution up into the cell. Then, the valve 22 is closed and the barrel 24 is raised to a point where the bottom of the barrel 24 is just below the surface of the solution 38 in base container 36. This traps a column of the solution in barrel 24 up to level 32. This makes it possible to measure the amount of gas evolved by noting the change in level 32 in the barrel 24. Subsequently, barrel 24 can be re-lowered into the container 36 of solution and the valve 22 opened to release the gasses produced. Then, the valve 22 is closed, the cell 24 raised, and the system is ready for further operation.

An alternative embodiment 40 of the inventive electrolysis apparatus is depicted in FIGS. 3 and 4. Inventive apparatus 40 comprises: an array of anode rods (e.g., wires) 42; a sheet of blacked cathodic material 48; a preferably transparent barrier membrane 44, positioned between anode array 42 and the blacked surface of cathode 48, which will allow free flow of ions, but not bubbles 46 of H₂ gas; and a transparent window 50 that allows light, preferably visible and ultraviolet, to pass therethrough to the blacked surface of cathode 48. The upper portion 52 of barrier 44 is preferably impermeable to gas to maintain separation between the hydrogen and oxygen produced.

For simplicity, the external electrical components of inventive apparatus 40 are not shown in FIGS. 4 and 5. Window 50 can be formed of glass. However, because much solar energy comes in the form of ultraviolet light which is largely absorbed by glass, it is preferred that the light admitting portions of the inventive cell be constructed of quartz, polymers, or other materials which will facilitate the transmission of UV light into the interior of the cell.

In the embodiment 20 of the inventive electrolysis apparatus depicted in FIG. 3, no effort is made to separate the hydrogen and oxygen gasses produced. However, it should be clear that cell 20 could be modified to allow for separation of the gasses produced. For example, a permeable or semi-permeable membrane, or even a thin, fine mesh sheet which could trap bubbles, but let light and the solution pass-through, could be used.

The electrolyte solution 38 employed in the inventive electrolysis system is most preferably a dilute solution of sulfuric acid (H₂SO₄) in water at a pH in the range of from

about 0.5 to about 7. The solution 38 will most preferably have a pH of about 2. Of course, other inorganic and organic acids may be equally useful, as would many neutral salt solutions such as solutions of sodium sulfate (Na_2SO_4). Some salts such as sodium chloride may be less useful because of the generation of other gasses in the system that might be corrosive to the electrodes. Further, some magnesium or aluminum salts can form gels under certain conditions of pH, which would render the cell less conductive, less efficient, and perhaps even opaque (i.e., thereby blocking access of light to the cathode). Under some circumstances, alkaline electrolyte solutions (i.e. above pH 7) may be preferable. The main requirements are that the solutions be relatively conductive and not be overly corrosive to the electrodes under the electrolysis conditions, or opaque to light.

Examples of suitable electrolytes include: lithium, sodium, potassium, magnesium or beryllium, salts, specifically, sulfates, hydroxides, or fluorides, the main requirement being that the electrolyte solution be conductive, have only limited, and preferably no, absorbence of the incident light, and not interfere with the photo-assisted electrochemistry occurring at the electrodes.

Current for both the electroplating and the photo-assisted electrolysis is preferably provided by a standard commercial transformer 6, 55 of the type sold as a battery replacement. This could be replaced by batteries or almost any other source of DC current. For test and development purposes it is convenient to be able to vary the current and voltage. However, once an optimum is determined for a given cell, geometry and construction capability to vary the current should not be essential, but could be useful. For testing, it may also be desirable to use a standard meter to measure the voltages, current flow or amperage, and/or resistance of the cell or whole system, at various points before, during and after the experiment.

An overarching goal of this instant invention is to use solar energy—especially visible and ultraviolet light—to assist in the electrolysis of water. For testing purposes, the instant inventors have used a common "high intensity" table lamp generally available commercially, although many other light sources could have been selected in the alternative. It should be noted that this source is relatively poor in high energy UV light and rich in lower energy visible light photons.

One of the distinguishing characteristics of this invention is the ability to use visible light efficiently. If desired, filters could be used in to modify the light striking the cathode surface, or lenses or mirrors could be used to concentrate, reflect, or direct the light to optimum impact on the cathode. Further, where it would be advantageous to do so, narrow band or monochromatic light sources could be used.

EXAMPLE

Using an electroplating apparatus 1 as depicted in FIGS. 1 and 2, a cathode 2 was formed and electroplated with nickel. The DC power supply employed in the experimental system included a plug-in transformer and a variable resistor. A 5¢ nickel coin was used as the electroplating anode 8. The anode 8 and cathode 2 were connected to the power source using insulated copper wires 4 and 10 and alligator clips. Cathode 2 was formed from copper foil shaped as a half cylinder having a diameter substantially equal to that of a syringe barrel 24 to be used in the next stage of the test. The bath 5 employed in the electroplating process comprised one-half teaspoon NiCl_2 per 30 ml of water. The transformer

was set at 4.5 V 300 m A and the nickel coin was moved back and forth over the inside surface of the copper cathode until the inside surface was fully and evenly electroplated with a micro-crystalline nickel layer. At the completion of the electroplating process, the cathode 2 was removed and rinsed with tap water.

Next, cathode 2 was employed in an electrolysis process using an electrolysis system as depicted in FIG. 5. The anode 28 used was a nichrome wire. The electrolyte 38 was an aqueous sulphuric acid solution having a pH of 2. Cathode 2 and anode 28 were held in place in syringe barrel 24 using a cork having holes formed therethrough to allow free movement of the electrolyte solution. The power source was linked to the cathode by means of an insulated copper wire soldered to the end of the cathode. The light source 34 employed in the test was an American Optical #655 lamp. The system 20 was tested with the light source 34 both on and off and using red, green, and blue dichroic additive filters. The system was also tested at various voltage differentials and with no input provided from the external power source. In each test, the syringe 34 was partially filled with electrolyte solution in the manner described above and the volume of solution in the syringe was recorded. The system was then operated for five minutes and the amount of hydrogen and oxygen gas generated in the test was determined by comparing the fluid volume in the syringe after the test to the fluid volume at the beginning of the test.

In these tests, no gas evolution was observed until the light source was turned on. The instant inventors also observed that lower voltages were required to produce electrolysis when the light was "ON" than under similar conditions when it was "OFF".

We believe that the observed increase in efficiency is related to the photoelectric effect as described by Albert Einstein where the energy of an electron emitted by a metal when struck by a photon of light is described by the equation:

$$E = h\nu - w$$

where E is the energy of the electron, h is Planck's constant, ν is the frequency of the incident light, and w is the work function of the metal. In general, the photoelectric effect is described using ultraviolet light which is of higher energy than visible light. Visible light generally does not have sufficient energy to give to an electron to enable it to reduce a hydrogen ion in solution to hydrogen gas. However, this limitation is overcome for purposes of the instant invention by creating an electrical potential between the anode and cathode.

The application of an electrical potential to the electrode modifies the previous equation to read as follows:

$$E = h\nu - w + P$$

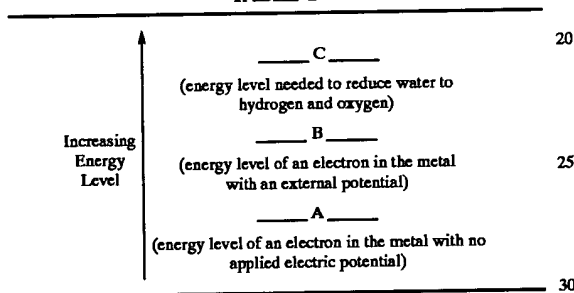
where P is the energy associated with the externally imposed electric field.

Essentially, according to our theory of operation, photon energy is used to boost the energy of an electron from the cathode up to the energy level needed for electrolysis. From this it follows that the wavelength of light required to generate photolysis is related to the external electric field. As the field strength (voltage) increases, the minimum energy of photons needed to generate electrolysis drops into the visible range. With no external electrical field, only photons with high energy relative to visible light give the electrons enough energy to split water into its component hydrogen and oxygen. As the external electric potential increases, the

minimum energy of a photon needed to split water drops into the visible spectrum, and potentially lower.

This is graphically depicted in Table 1. As illustrated in Table 1, the external potential on the electrodes provides the electron energy to go from A (energy level with no applied electric potential) to B (energy level with electric potential applied) but the electron does not have the energy to electrolyze water until that energy is provided by the photon of light. In other words, the energy A-C is the total needed for electrolysis, the energy A-B is provided by the externally imposed potential on the electrodes, and the energy B-C is provided by the light photons. The energy level B varies, increasing with increased imposed external potential. As the potential is raised, the additional photon energy required for electrolysis is reduced, enabling the capture and use of a larger portion of the incident light.

TABLE 1



Since, according to the photoelectric effect, a photon imparts energy to a single electron, the number of photons needed of above the minimum energy level is (within limits imposed by the cell design) directly proportional to the number of electrons produced and the amount of hydrogen and oxygen produced. In other words, the more intense the light, the more hydrogen will be produced, all other things being equal. However, the production of hydrogen can also be limited by the number of electrons available at the cathode, or the flow of electrons, or the electrical current.

In contrast to other systems heretofore contemplated, it is preferred that neither the cathode nor the anode employed in the inventive electrolysis apparatus include any semiconductor materials. The inventive apparatus will operate at voltages lower than 2.0, although such operation may be a less efficient use of the photoenergy. Additionally, in the instant invention, it is not necessary (but may be desirable) to add resistance to the circuit formed by the cathode and anode, other than the resistance that naturally occurs in the cell. Further, the instant invention uses light to energize the electrons in the cathode metal, rather than to ionize the electrolyte solution. The inventive system preferably uses the cathode to capture light and act as a surface for electrolysis.

While the inventive device has been described and illustrated herein by reference to certain preferred embodiments in relation to the drawings attached hereto, various changes and further modifications, apart from those shown or suggested herein, may be made therein by those skilled in the art, without departing from the spirit of the inventive concept, the scope of which is to be determined by the following claims.

What is claimed is:

1. An apparatus for photoelectrolysis comprising:
 - a container;
 - a cathode positioned in said container; and

an anode positioned in said container,
said container being operable to allow transmission of light to said cathode from a light source external to said container,

said cathode comprising a sheet of conductive metal blacked with a layer of conductive metal disposed on one side of said sheet of conductive metal in a manner such that said layer of conductive metal is operable for both absorbing said light and for acting as a cathodic surface for electrolysis, and

said anode being an array of rods positioned adjacent said layer of conductive metal.

2. An apparatus for photoelectrolysis comprising:

a container;

a cathode positioned in said container; and

an anode positioned in said container;

said container being operable to allow transmission of light to said cathode from a light source external to said container,

said cathode comprising a sheet of conductive metal blacked with a layer of conductive metal in a manner such that said layer of conductive metal is operable for both absorbing said light and for acting as a cathodic surface for electrolysis, and

said sheet of conductive metal being formed in a shape of a partial cylinder having an inside surface and wherein said inside surface has been blacked with said layer of conductive metal.

3. The apparatus of claim 2 wherein said anode is an elongate member positioned adjacent said inside surface such that all points of said inside surface are substantially equidistant from said anode.

4. An apparatus for photo-assisted electrolysis comprising:

a cathode effective both for collecting light energy to assist said electrolysis and for acting as an electrode for said electrolysis;

an anode; and

an external electrical power source electrically connected to said cathode and to said anode such that said external electrical power source is effective for establishing an electrical potential between said cathode and said anode.

5. The apparatus of claim 4 wherein said external electrical power source is effective for establishing a sufficient electrical potential between said cathode and said anode such that light energy in the visible spectrum collected by said cathode will assist said electrolysis.

6. The apparatus of claim 4 wherein said cathode includes no semiconductor materials.

7. The apparatus of claim 4 wherein said anode includes no semiconductor materials.

8. The apparatus of claim 4 wherein said cathode comprises a base of conductive metal blacked with a layer of conductive metal in manner such that said layer of conductive metal is effective for both absorbing light and acting as a cathode surface for said electrolysis.

9. The apparatus of claim 8 wherein said base has been blacked by electroplating a surface of said base to form said layer of conductive metal thereon.

10. The apparatus of claim 8 wherein said cathode consists essentially of only said base and said layer of conductive metal and wherein said base and said layer of conductive metal include no semiconductor materials.

11. The apparatus of claim 8 wherein said base consists essentially of a metal, in elemental form, selected from the

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group consisting of: copper, nickel, tin, silver, gold, platinum, palladium, graphite, graphite carbon, iron, chromium, manganese, titanium, and alloys thereof.

12. The apparatus of claim 11 wherein said base is formed of copper.

13. The apparatus of claim 8 wherein said layer of conductive metal consists essentially of a metal, in elemental form, selected from the group consisting of nickel, platinum, palladium, and cobalt.

14. The apparatus of claim 13 wherein said layer of conductive metal is formed of nickel.

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15. The apparatus of claim 8 further comprising a container wherein said cathode and said anode are positioned, said container being effective for allowing transmission of light therethrough to said cathode from a light source external to said container.

16. The apparatus of claim 15 further comprising an acidic electrolyte in said container, said cathode and said anode being positioned in said acidic electrolyte.

* * * * *



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(12) **United States Patent**
Chen

(10) Patent No.: **US 6,290,833 B1**
(45) Date of Patent: **Sep. 18, 2001**

(54) **METHOD FOR ELECTROLYTICALLY
DEPOSITING COPPER ON A
SEMICONDUCTOR WORKPIECE**

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(73) Assignee: **Semitool, Inc., Kalispell, MT (US)**

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/387,033**

(22) Filed: **Aug. 31, 1999**

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(63) Continuation of application No. PCT/US99/06306, filed on Mar. 22, 1999, which is a continuation of application No. 09/045,245, filed on Mar. 20, 1998, now Pat. No. 6,197,181.

(60) Provisional application No. 60/085,675, filed on May 15, 1998.

(51) Int. Cl.⁷ **C25D 5/10**

(52) U.S. Cl. **205/182; 205/170; 205/296**

(58) Field of Search **205/291, 296,
205/123, 125, 157, 170, 182**

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(57) ABSTRACT

This invention employs a novel approach to the copper metallization of a workpiece, such as a semiconductor workpiece. In accordance with the invention, an alkaline electrolytic copper bath is used to electroplate copper onto a seed layer, electroplate copper directly onto a barrier layer material, or enhance an ultra-thin copper seed layer which has been deposited on the barrier layer using a deposition process such as PVD. The resulting copper layer provides an excellent conformal copper coating that fills trenches, vias, and other microstructures in the workpiece. When used for seed layer enhancement, the resulting copper seed layer provide an excellent conformal copper coating that allows the microstructures to be filled with a copper layer having good uniformity using electrochemical deposition techniques. Further, copper layers that are electroplated in the disclosed manner exhibit low sheet resistance and are readily annealed at low temperatures.

27 Claims, 10 Drawing Sheets

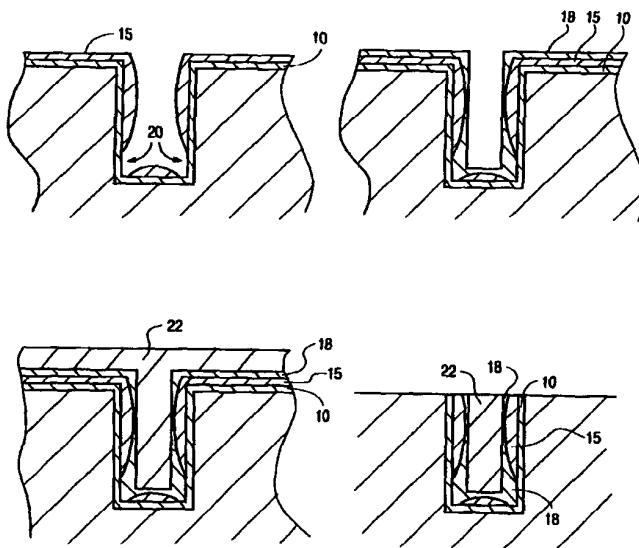


Fig. 1

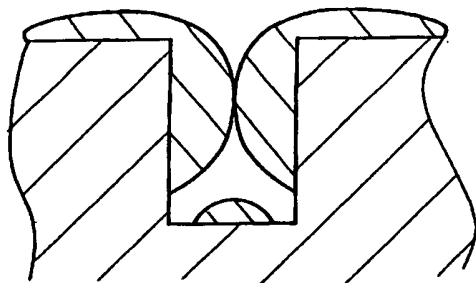


Fig. 2A

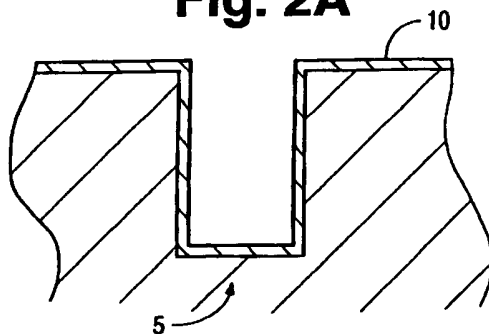


Fig. 2B

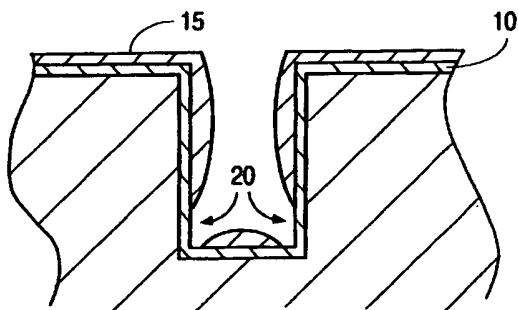


Fig. 2C

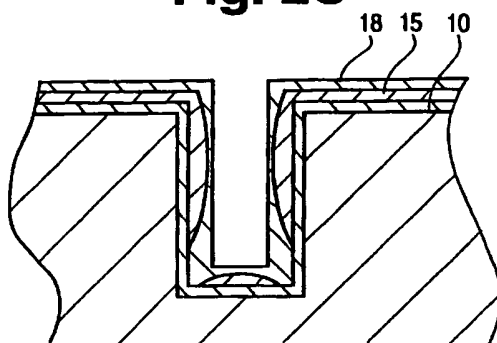


Fig. 2D

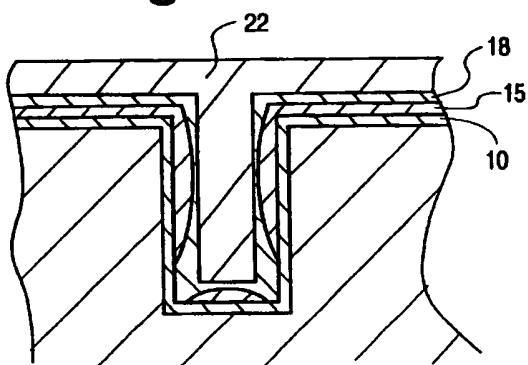


Fig. 2E

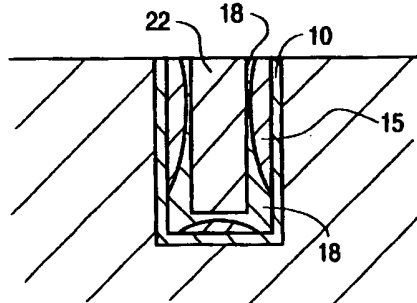
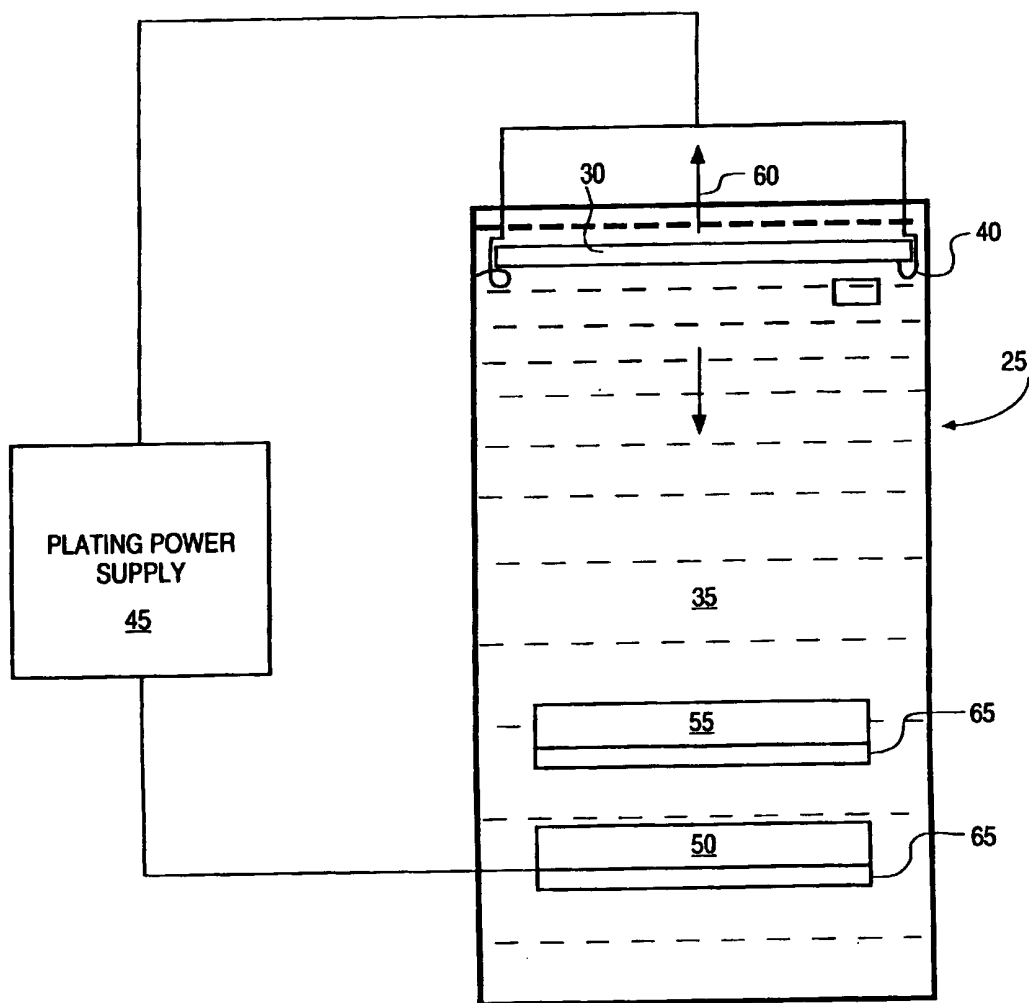
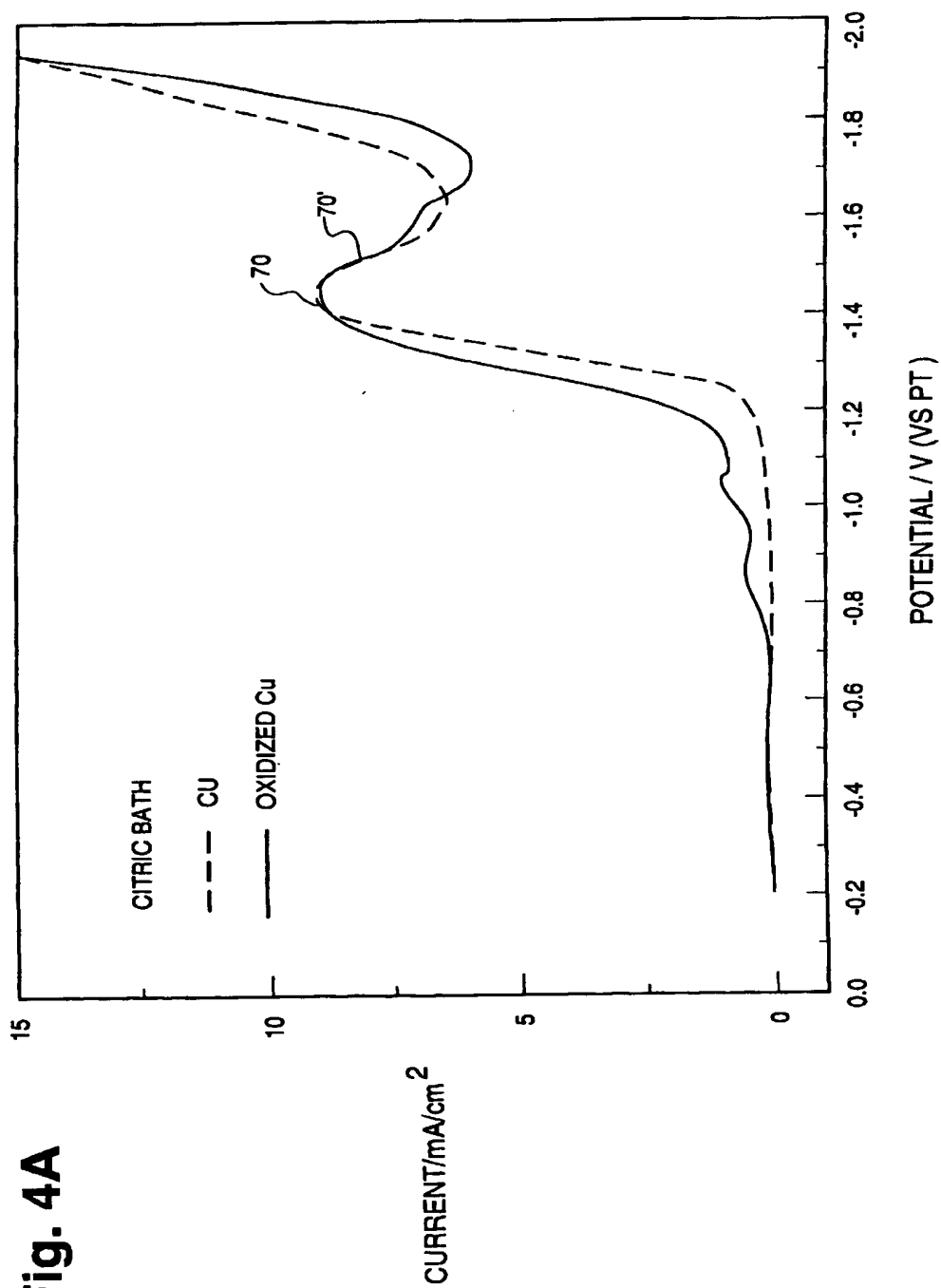
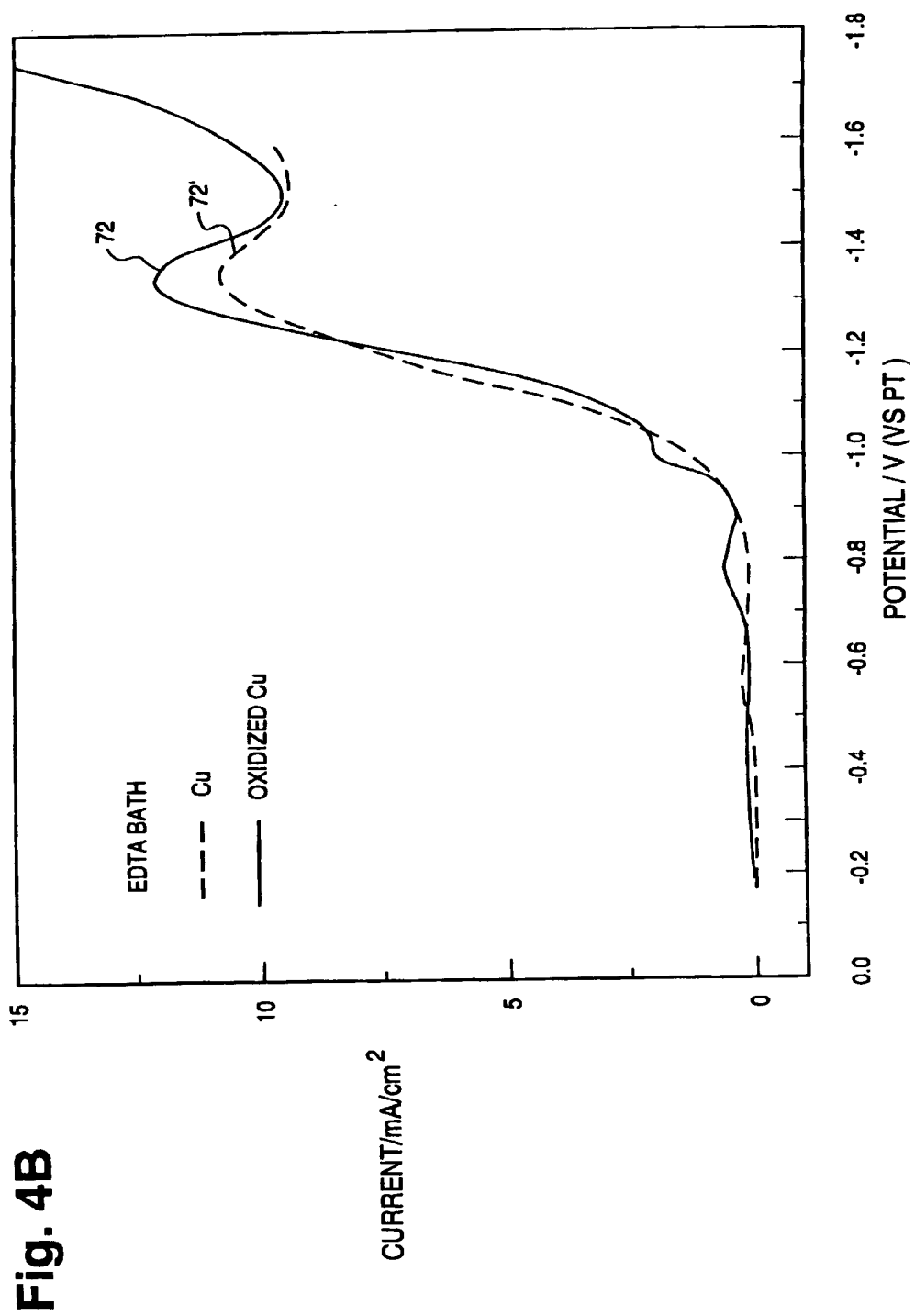
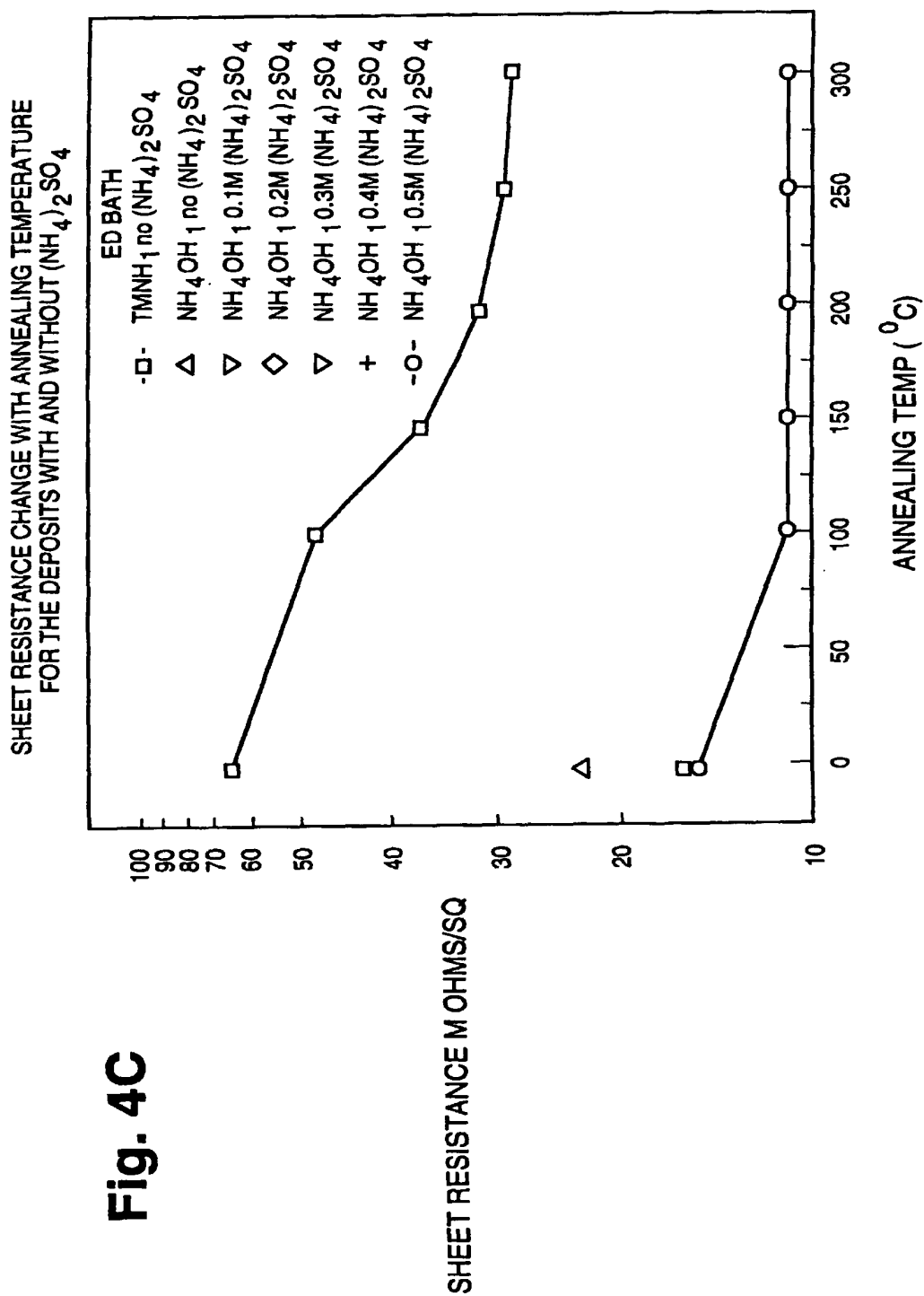


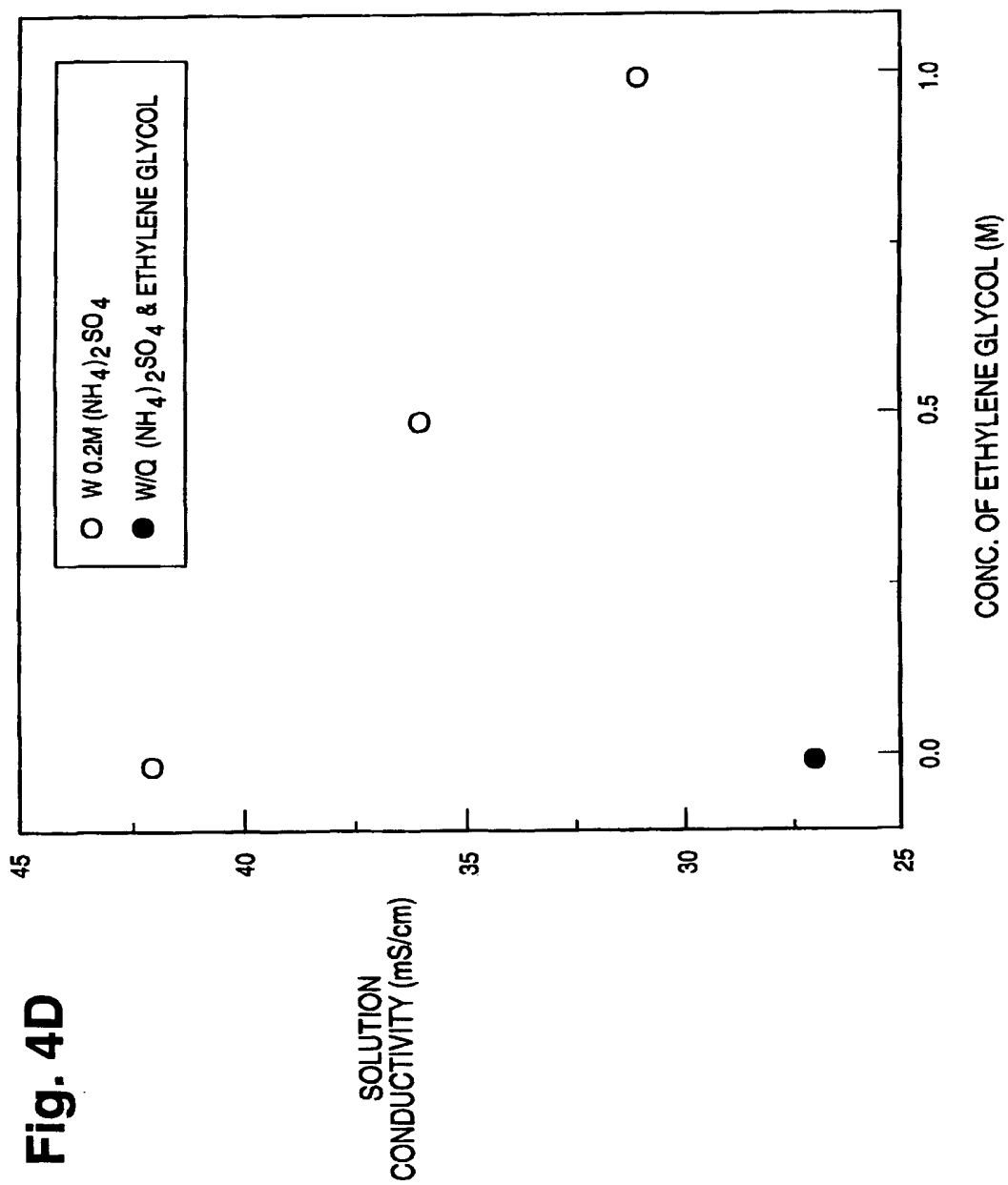
Fig. 3











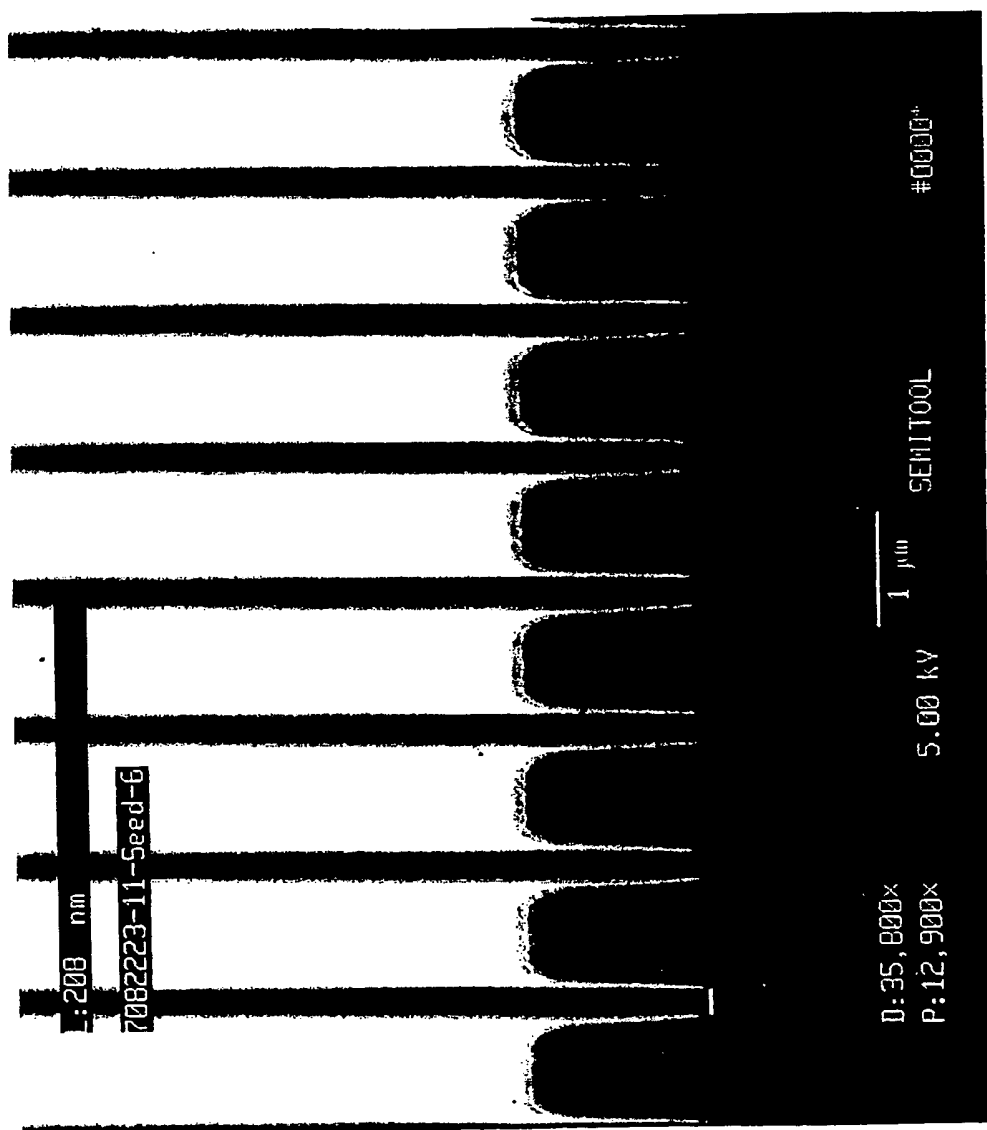


Fig. 5

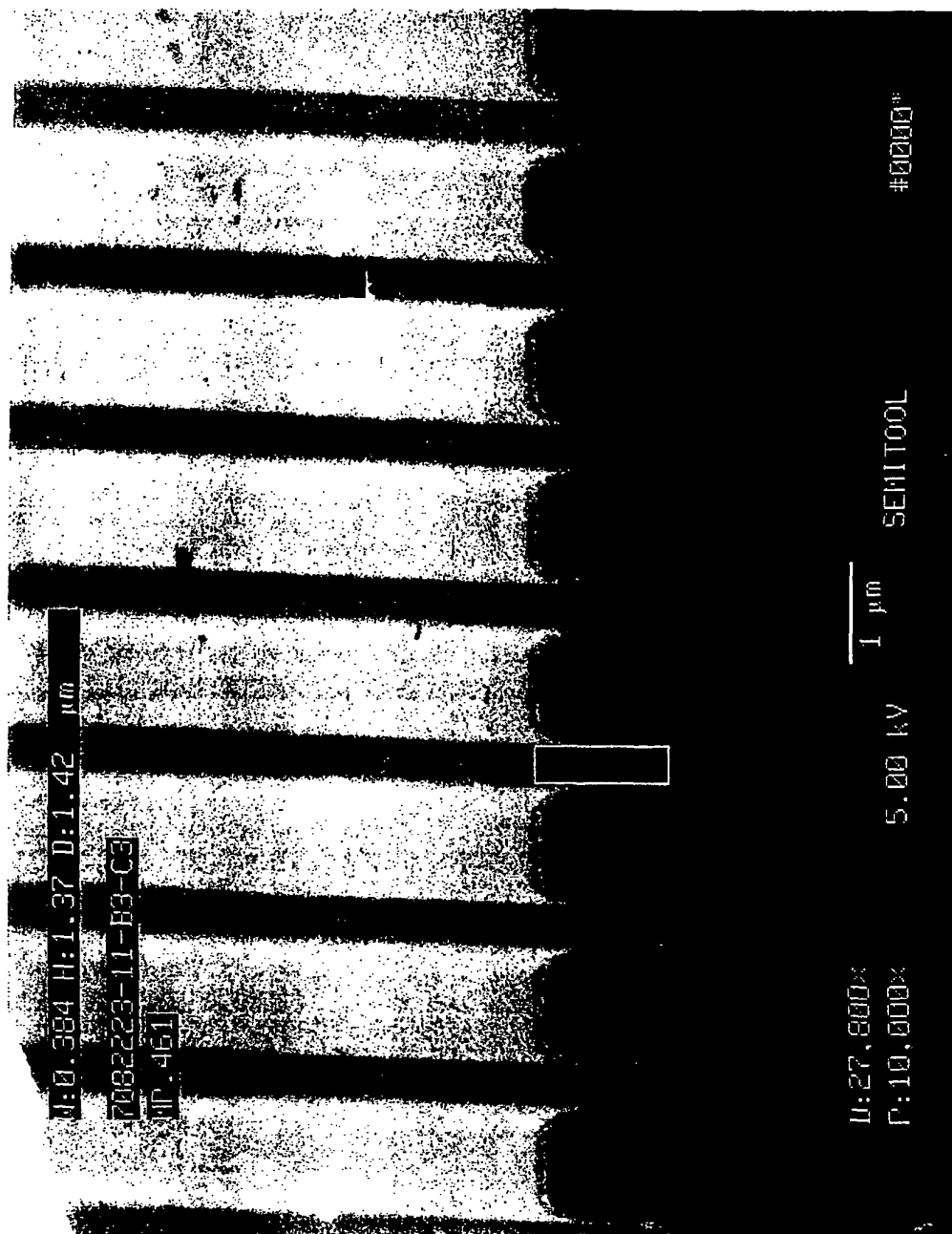


Fig. 6A

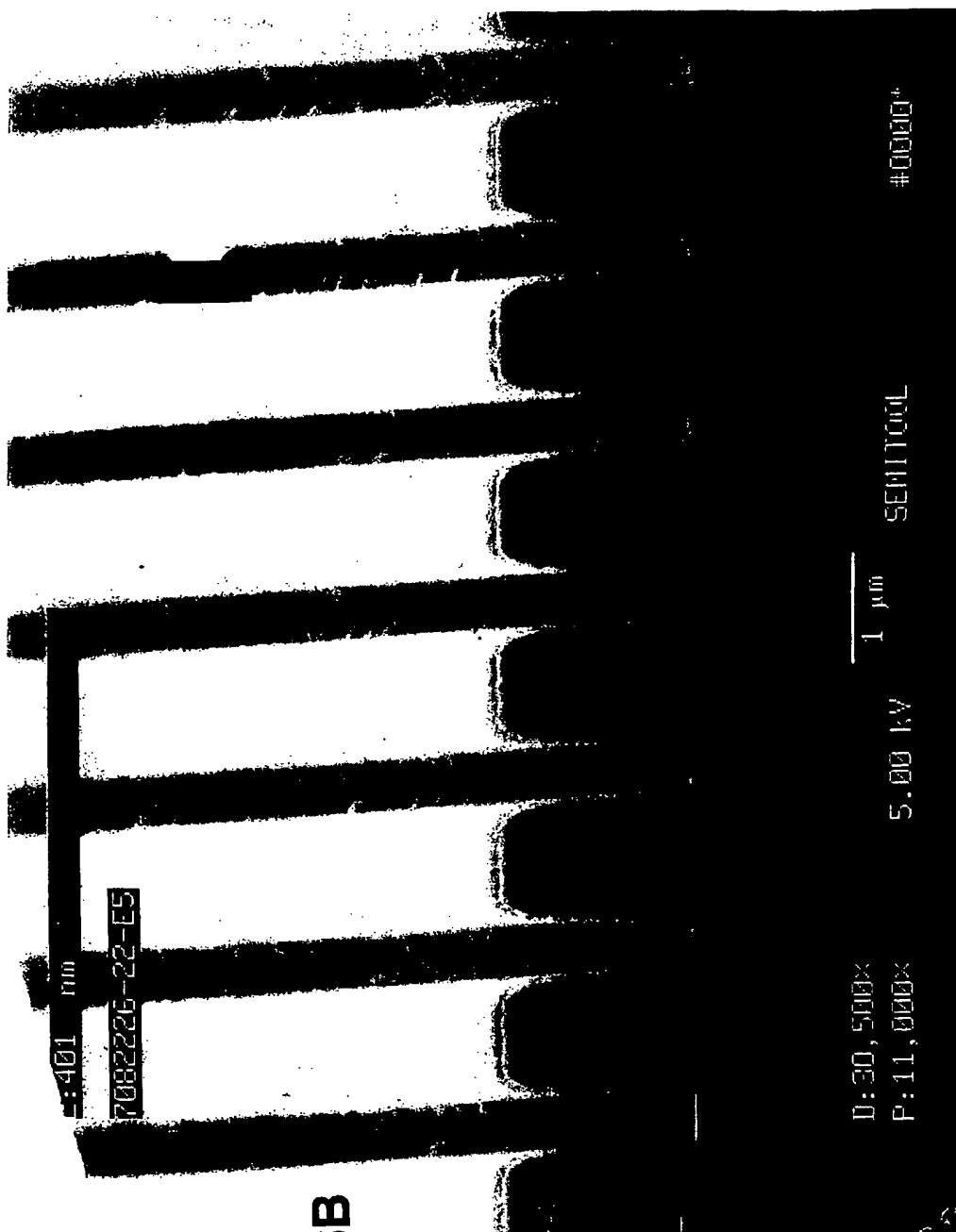
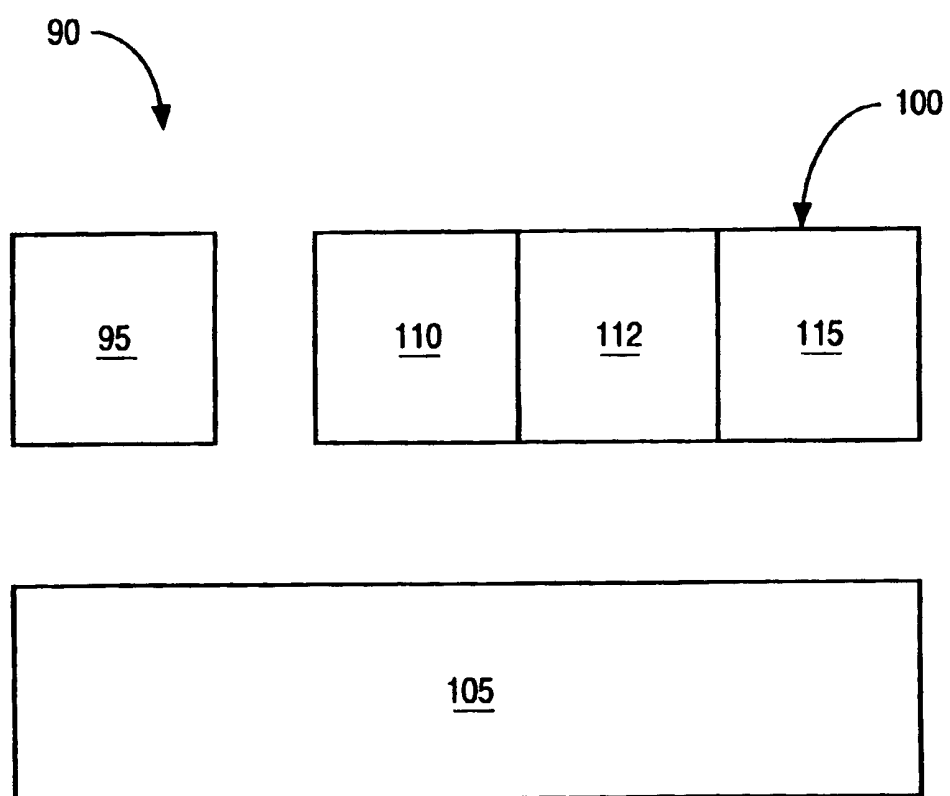


Fig. 6B

Fig. 7

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METHOD FOR ELECTROLYTICALLY DEPOSITING COPPER ON A SEMICONDUCTOR WORKPIECE

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation application of International PCT Patent Application No. PCT/US99/06306, designating the US, filed Mar. 22, 1999, entitled APPARATUS AND METHOD FOR ELECTROLYTICALLY DEPOSITING COPPER ON A SEMICONDUCTOR WORKPIECE, which continuation U.S. patent application Ser. No. 09/045,245, filed Mar. 20, 1998, now U.S. Pat. No. 6,197,181, and U.S. patent application Ser. No. 60/085,675, filed May 15, 1998.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not Applicable

BACKGROUND OF THE INVENTION

In the fabrication of microelectronic devices, application of one or more metallization layers is often an important step in the overall fabrication process. The metallization may be used in the formation of discrete microelectronic components, such as read/write heads, but it is more often used to interconnect components formed on a workpiece, such as a semiconductor workpiece. For example, such structures are used to interconnect the devices of an integrated circuit.

A basic understanding of certain terms used herein will assist the reader in understanding the disclosed subject matter. To this end, basic definitions of certain terms, as used in the present disclosure, are set forth below.

Single Metallization Level is defined as a composite level of a workpiece that is exterior to the substrate. The composite level comprises one or more metal structures.

Substrate is defined as a base layer of material over which one or more metallization levels are disposed. The substrate may be, for example, a semiconductor wafer, a ceramic block, etc.

Workpiece is defined as an object that at least comprises a substrate, and may include further layers of material or manufactured components, such as one or more metallization levels, disposed on the substrate.

An integrated circuit is an interconnected ensemble of devices formed within a semiconductor material and within a dielectric material that overlies a surface of the semiconductor. Devices which may be formed within the semiconductor include MOS transistors, bipolar transistors, diodes and diffused resistors. Devices which may be formed within the dielectric include thin-film resistors and capacitors. Typically, more than 100 integrated circuit die (IC chips) are constructed on a single 8 inch diameter silicon wafer. The devices utilized in each dice are interconnected by conductor paths formed within the dielectric. Typically, two or more levels of conductor paths, with successive levels separated by a dielectric layer, are employed as interconnections. In current practice, an aluminum alloy and silicon oxide are typically used for, respectively, the conductor and dielectric.

Delays in propagation of electrical signals between devices on a single die limit the performance of integrated circuits. More particularly, these delays limit the speed at which an integrated circuit may process these electrical signals. Larger propagation delays reduce the speed at which

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the integrated circuit may process the electrical signals, while smaller propagation delays increase this speed. Accordingly, integrated circuit manufacturers seek ways in which to reduce the propagation delays.

For each interconnect path, signal propagation delay may be characterized by a time delay τ . See E. H. Stevens, *Interconnect Technology*, QMC, Inc., July 1993. An approximate expression for the time delay, τ , as it relates to the transmission of a signal between transistors on an integrated circuit is given below.

$$\tau = RC[1 + (V_{SAT}/RI_{SAT})]$$

In this equation, R and C are, respectively, an equivalent resistance and capacitance for the interconnect path and I_{SAT} and V_{SAT} are, respectively, the saturation (maximum) current and the drain-to-source potential at the onset of current saturation for the transistor that applies a signal to the interconnect path. The path resistance is proportional to the resistivity, ρ , of the conductor material. The path capacitance is proportional to the relative dielectric permittivity, K_e , of the dielectric material. A small value of τ requires that the interconnect line carry a current density sufficiently large to make the ratio V_{SAT}/RI_{SAT} small. It follows therefore, that a low- ρ conductor which can carry a high current density and a low- K_e dielectric must be utilized in the manufacture of high-performance integrated circuits.

To meet the foregoing criterion, copper interconnect lines within a low- K_e dielectric will likely replace aluminum-alloy lines within a silicon oxide dielectric as the most preferred interconnect structure. See "Copper Goes Mainstream: Low-k to Follow", *Semiconductor International*, November 1997, pp. 67-70. Resistivities of copper films are in the range of 1.7 to 2.0 $\mu\Omega\text{cm}$; resistivities of aluminum-alloy films are in the range of 3.0 to 3.5 $\mu\Omega\text{cm}$.

Despite the advantageous properties of copper, it has not been as widely used as an interconnect material as one would expect. This is due, at least in part, to the difficulty of depositing copper metallization and, further, due to the need for the presence of barrier layer materials. The need for a barrier layer arises from the tendency of copper to diffuse into silicon junctions and alter the electrical characteristics of the semiconductor devices formed in the substrate. Barrier layers made of, for example, titanium nitride, tantalum nitride, etc., must be laid over the silicon junctions and any intervening layers prior to depositing a layer of copper to prevent such diffusion.

A number of processes for applying copper metallization to semiconductor workpieces have been developed in recent years. One such process is chemical vapor deposition (CVD), in which a thin copper film is formed on the surface of the barrier layer by thermal decomposition and/or reaction of gas phase copper compositions. A CVD process can result in conformal copper coverage over a variety of topological profiles, but such processes are expensive when used to implement an entire metallization layer.

Another known technique, physical vapor deposition (PVD), can readily deposit copper on the barrier layer with relatively good adhesion when compared to CVD processes. One disadvantage of PVD processes, however, is that they result in poor (non-conformal) step coverage when used to fill microstructures, such as vias and trenches, disposed in the surface of the semiconductor workpiece. For example, such non-conformal coverage results in less copper deposition at the bottom and especially on the sidewalls of trenches in the semiconductor devices.

Inadequate deposition of a PVD copper layer into a trench to form an interconnect line in the plane of a metallization

layer is illustrated in FIG. 1. As illustrated, the upper portion of the trench is effectively "pinched off" before an adequate amount of copper has been deposited within the lower portions of the trench. This results in an open void region that seriously impacts the ability of the metallization line to carry the electrical signals for which it was designed.

Electrochemical deposition of copper has been found to provide the most cost-effective manner in which to deposit a copper metallization layer. In addition to being economically viable, such deposition techniques provide substantially conformal copper films that are mechanically and electrically suitable for interconnect structures. These techniques, however, are generally only suitable for applying copper to an electrically conductive layer. As such, an underlying conductive seed layer is generally applied to the workpiece before it is subject to an electrochemical deposition process. Techniques for electrodeposition of copper on a barrier layer material have not heretofore been commercially viable.

The present inventors have recognized that there exists a need to provide copper metallization processing techniques that 1) provide conformal copper coverage with adequate adhesion to the barrier layer, 2) provide adequate deposition speeds, and 3) are commercially viable. These needs are met by the apparatus and processes of the present invention as described below.

BRIEF SUMMARY OF THE INVENTION

This invention employs a novel approach to the copper metallization of a workpiece, such as a semiconductor workpiece. In accordance with the invention, an alkaline electrolytic copper bath is used to electroplate copper onto a seed layer, electroplate copper directly onto a barrier layer material, or enhance an ultra-thin copper seed layer which has been deposited on the barrier layer using a deposition process such as PVD. The resulting copper layer provides an excellent conformal copper coating that fills trenches, vias, and other microstructures in the workpiece. When used for seed layer enhancement, the resulting copper seed layer provides an excellent conformal copper coating that allows the microstructures to be filled with a copper layer having good uniformity using electrochemical deposition techniques. Further, copper layers that are electroplated in the disclosed manner exhibit low sheet resistance and are readily annealed at low temperatures.

The disclosed process, as noted above, is applicable to a wide range of steps used in the manufacture of a metallization layer in a workpiece. The workpiece may, for example, be a semiconductor workpiece that is processed to form integrated circuits or other microelectronic components. Without limitation as to the applicability of the disclosed invention, a process for enhancing a seed layer is described.

A process for applying a metallization interconnect structure to a workpiece having a barrier layer deposited on a surface thereof is also set forth. The process includes the forming of an ultra-thin metal seed layer on the barrier layer. The ultra-thin seed layer has a thickness of less than or equal to about 500 Angstroms and may be formed from any material that can serve as a seed layer for subsequent metal deposition. Such metals include, for example, copper, copper alloys, aluminum, aluminum alloys, nickel, nickel alloys, etc. The ultra-thin seed layer is then enhanced by depositing additional metal thereon in a separate deposition step to provide an enhanced seed layer that is suitable for use in a primary metal deposition. The enhanced seed layer has a thickness at all points on sidewalls of substantially all recessed features distributed within the workpiece that is

equal to or greater than about 10% of the nominal seed layer thickness over an exteriorly disposed surface of the workpiece.

In accordance with a specific embodiment of the process, a copper-containing metallization interconnect structure is formed. To this end, the ultra-thin seed layer is enhanced by subjecting the semiconductor workpiece to an electrochemical copper deposition process in which an alkaline bath having a complexing agent is employed. The copper complexing agent may be at least one complexing agent selected from a group consisting of EDTA, ED, and a polycarboxylic acid such as citric acid or salts thereof.

Various plating bath compositions suitable for blanket plating, fill-plating of recessed micro-structures, and seed layer enhancement plating are also set forth. A preferred solution for electroplating copper for seed layer enhancement comprises copper sulfate, boric acid, and a complexing agent. The complexing agent is preferably selected from the group consisting of ED, EDTA, and a polycarboxylic acid, such as citric acid. This solution is also suitable for blanket plating and fill-plating of recessed micro-structures.

A plating solution that improves the resistivity of the resulting copper film is also set forth. The plating solution preferably comprises copper sulfate, ammonium sulfate, and ethylene glycol. This solution is also suitable for blanket plating and fill-plating of recessed micro-structures.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

FIG. 1 is a cross-sectional view illustrating an interconnect line formed completely by PVD copper.

FIGS. 2A-2E are cross-sectional views through a semiconductor workpiece illustrating the various layers of material as they are applied in accordance with one embodiment of the present invention.

FIG. 3 is a schematic representation of an apparatus suitable for enhancing an ultra-thin seed layer.

FIG. 4A is a graph illustrating the current-potential curves of a plating solution using a polycarboxylic acid, such as citric acid, as a complexing agent.

FIG. 4B is a graph illustrating the current-potential curves of a plating solution using EDTA, an amine-containing plating solution, as the complexing agent.

FIG. 4C is a graph of sheet resistance change with annealing temperature for copper films deposited from a bath solution with and without ammonium sulfate.

FIG. 4D is a graph illustrating plating solution conductivity as a function of ethylene glycol concentration in collating solutions with and without ammonium sulfate.

FIG. 5 is a scanning electron micrograph photograph illustrating an ultra-thin seed layer.

FIG. 6A is a scanning electron micrograph photograph illustrating an ultra-thin seed layer that has been enhanced in a citric acid bath.

FIG. 6B is a scanning electron micrograph photograph illustrating an ultra-thin seed layer that has been enhanced in an EDTA bath.

FIG. 7 is a schematic representation of a section of a semiconductor manufacturing line suitable for implementing the disclosed seed layer enhancement steps.

DETAILED DESCRIPTION OF THE INVENTION

This invention employs a novel approach to applying copper metallization to a workpiece, such as a semiconduc-

tor workpiece. In accordance with the invention, an alkaline electrolytic copper bath is used to electroplate copper onto a seed layer, electroplate copper directly onto a barrier layer material, or enhance an ultra-thin copper seed layer which has been deposited on the barrier layer using a deposition process such as PVD. Additionally, a method for applying a metallization layer will be disclosed. Although the disclosed method may be used in connection with a substantial number of different metal compositions, the specific embodiment disclosed herein is directed to the application of a copper-containing metallization layer. To this end, an alkaline electrolytic copper bath is used to enhance an ultra-thin copper seed layer which has been deposited on a barrier layer using a deposition process such as PVD. The enhanced copper seed layer provides an excellent conformal copper coating that allows trenches and vias to be subsequently filled with a copper layer having good uniformity using electrochemical deposition techniques.

A cross-sectional view of a micro-structure, such as trench 5, that is to be filled with copper metallization is illustrated in FIG. 2A and will be used to describe the seed layer enhancement aspects of the present invention. As shown, a thin barrier layer 10 of, for example, titanium nitride or tantalum nitride is deposited over the surface of a semiconductor device or, as illustrated in FIG. 2A, over a layer of a dielectric 8, such as silicon dioxide. The barrier layer 10 acts to prevent the migration of copper to any semiconductor device formed in the substrate. Any of the various known techniques, such as CVD or PVD, can be used to deposit the barrier layer depending on the particular barrier material being used. Preferably, the thickness for the barrier layer is approximately 100 to 300 Angstroms.

After the deposition of the barrier layer, an ultra-thin copper seed layer 15 is deposited on the barrier layer 10. The resulting structure is illustrated in FIG. 2B. Preferably, the copper seed layer 15 is formed using a vapor deposition technique, such as CVD or PVD. In order to have adequate adhesion and copper coverage, a relatively thick (1000 Angstroms) copper seed layer is usually required. Such a thick seed layer leads to problems with close-off of small geometry trenches, however, when a PVD deposition process is employed for applying the seed layer.

Contrary to traditional thoughts regarding seed layer application, the copper seed layer 15 of the illustrated embodiment is ultra-thin, having a thickness of about 50 to about 500 Angstroms, preferably about 100 to about 250 Angstroms, and most preferably about 200 Angstroms. The ultra-thin copper seed layer can be deposited using a CVD or a PVD process, or a combination of both. PVD is the preferred application process, however, because it can readily deposit copper on the barrier layer 10 with relatively good adhesion. By depositing an ultra-thin seed layer of copper, rather than the relatively thick seed layer used in the prior art, pinching off of the trenches can be avoided.

The use of an ultra-thin seed layer 15 generally introduces its own set of problems. One of the most significant of these problems is the fact that such ultra-thin layers do not generally coat the barrier layer 10 in a uniform manner. Rather, voids or non-continuous seed layer regions on the sidewalls, such as at 20, are often present in an ultra-thin seed layer 15 thereby resulting in the inability to properly apply a subsequent electrochemically deposited copper layer in the regions 20. Further, ultra-thin seed layers tend to include spikes, such as at 21, that impact the uniformity of the subsequent electrolytically deposited metal layer. Such spikes 21 result in high potential regions at which the copper deposits at a higher rate than at other, more level regions. As

such, the seed layer 15 is not fully suitable for the traditional electroplating techniques typically used after application of a seed layer.

The present inventors have found that an ultra-thin seed layer can be employed if it is combined with a subsequent electrochemical seed layer enhancement technique. To this end, the semiconductor workpiece is subject to a subsequent process step in which a further amount of copper 18 is applied to the ultra-thin seed layer to thereby enhance the seed layer. A seed layer enhanced by the additional deposition of copper is illustrated in FIG. 2C. As shown in FIG. 2C, the void or non-continuous regions 20 of FIG. 2B have been filled thereby leaving substantially all of the barrier layer 10 covered with copper.

Preferably, the seed layer enhancement process continues until a sidewall step coverage, i.e., the ratio of the seed layer thickness at the bottom sidewall regions 22 to the nominal thickness of the seed layer at the exteriorly disposed side 23 of the workpiece, achieves a value of at least 10%. More preferably, the sidewall step coverage is at least about 20%. Such sidewall step coverage values are present in substantially all of the recessed structures of the semiconductor workpiece. It will be recognized, however, that certain recessed structures distributed within the semiconductor workpiece may not reach these sidewall step coverage values. For example, such structures disposed at the peripheral edges of a semiconductor wafer may not reach these step coverage values. Similarly, defects or contaminants at the situs of certain recessed structures may prevent them from reaching the desired coverage values. The nominal thickness of the enhanced seed layer at the exteriorly disposed side of the workpiece is preferably in the range of 500 angstroms 1600 angstroms.

Although the embodiment of the process disclosed herein is described in connection with copper metallization, it is understood that the basic principle of the enhancement of an ultra-thin seed layer prior to the bulk deposition thereof can be applied to other metals or alloys that are capable of being electroplated. Such metals include iron, nickel, cobalt, zinc, copper-zinc, nickel-iron, cobalt-iron, etc.

A schematic representation of an apparatus 25 suitable for enhancing the ultra-thin copper seed layer is illustrated in FIG. 3. It will be recognized that this apparatus is also suitable for applying a blanket plating layer and/or full-fill plating of recessed micro-structures. As shown, a semiconductor workpiece, such as a semiconductor wafer 30, is positioned face down in a bath 35 of electroplating solution. One or more contacts 40 are provided to connect the wafer 30 to a plating power supply 45 as a cathode of an electroplating cell. An anode 50 is disposed in the bath 35 and is connected to the plating power supply 45. Preferably, a diffuser 55 is disposed between the anode 50 and the wafer/cathode 30. The wafer 30 may be rotated about axis 60 during the enhancement process. Anode 50 may be provided with a dielectric shield 65 at a backside thereof which faces an incoming stream of plating bath fluid.

As noted above, certain aspects of the present invention relate to new and useful plating solutions. These solutions can be used for blanket plating, full-fill of the recessed micro-structures, seed layer enhancement, etc. The preferred electrolytic bath solution for enhancing the seed layer is an alkaline copper bath in which copper ions are complexed with a complexing agent. A preferred composition and range of concentrations for the various components of the plating bath include the following:

1. Copper sulfate: 0.03M to 0.25M (preferably, 0.04);
2. Complexing agent: complex to metal ratios from 1 to 4, preferably 2;
3. Boric acid: 0.01M to 0.5M, preferably 0.05M; and
4. pH: 5–13, preferably 9.5.

A preferred source of copper ions is copper sulfate (CuSO_4). The concentration of copper sulfate in the bath is preferably within the range of 0.03 to 0.25 M, and is more preferably about 0.1 M.

Complexing agents that are suitable for use in the present invention form a stable complex with copper ions and prevent the precipitation of copper hydroxide. Ethylene diamine tetracetic acid (EDTA), ethylene diamine (ED), citric acid, and their salts have been found to be particularly suitable copper complexing agents. The molar ratio of complexing agent to copper sulfate in the bath is preferably within the range of 1 to 4, and is preferably about 2. Such complexing agents can be used alone, in combination with one another, or in combination with one or more further complexing agents.

The electrolytic bath is preferably maintained at a pH of at least 9.0. Potassium hydroxide, ammonium hydroxide, tetramethylammonium hydroxide, or sodium hydroxide is utilized to adjust and maintain the pH at the desired level of 9.0 or above. A preferred pH for a citric acid or ED bath is about 9.5, while a preferred pH for an EDTA bath is about 12.5. As noted above, the complexing agent assists in preventing the copper from precipitating at the high pH level.

Additional components can be added to the alkaline copper bath. For example, boric acid (H_3BO_3) aids in maintaining the pH at 9.5 when citric acid or ED is used as the complexing agent, and provides brighter copper deposits when added to an electrolytic bath containing EDTA as the complexing agent. If boric acid is added, its concentration in the bath is preferably within the range of 0.01 to 0.5 M.

In general, the temperature of the bath can be within the range of 20 to 35° C., with 25° C. being a preferred temperature. The current density for electrolytically depositing copper to enhance the copper seed layer can be 1 to 5 milliamperes/cm², while a plating time of about 1 to about 5 minutes is sufficient to enhance the copper seed layer. The plating waveform may be, for example, a forward periodic pulse having a period of 2 msec at a 50% duty cycle.

An amine free acid complexing agent, for example, a polycarboxylic acid, such as citric acid, and salts thereof, is preferable to the use of EDTA or ED. EDTA and ED include amine groups. These amine groups often remain on the surface of the semiconductor workpiece after rinsing and drying of the wafer. Subsequent processes, particularly such processes as photolithographic processes, may be corrupted by the reactions resulting from the presence of these amine groups. The amine groups may, for example, interfere with the chemical reactions associated with the exposing and/or curing of photoresist materials. As such, amine free complexing agents are particularly suitable in processes in which a photolithographic process follows an electrodeposition process.

A further advantage of using a polycarboxylic acid, such as citric acid, stems from the fact that the magnitude of the voltage potential at which the copper is plated is greater than the magnitude of the voltage potential at which the copper is plated in a bath containing EDTA. This is illustrated in FIGS. 4A and 4B where FIG. 4A is a current-potential graph for a citric acid bath, and FIG. 4B is a current-potential graph for an EDTA bath. Electroplating takes place at the voltage where the corresponding current increases abruptly.

This plating voltage is referred to as the deposition potential, which is approximately –1.25 volts as shown in FIG. 4A for a bath employing citric acid as the complexing agent, and is approximately –1.0 volts as shown in FIG. 4B for a bath employing EDTA as the complexing agent. The current peaks (70 70' for the bath containing a citric acid, and 72, 72' for the bath containing the EDTA) are the limiting currents which are mainly determined by mass transfer and the concentration of copper ions in the plating solutions. As illustrated, the magnitude of the current and the particular plating potential is slightly dependent on the substrate material. The different substrate results are illustrated in FIGS. 4A and 4B, where 70 and 72 are the curves for a copper substrate material, and 70' and 72' are curves for a copper substrate material comprised of copper with a copper oxide coating. It is noted that additional peaks occur on oxidized copper in the same electrolytes. These peaks are related to the electrochemical reduction of copper oxide to metallic copper before the alkaline electrochemical copper deposition.

It is believed that a copper layer plated at a higher plating potential in an alkaline bath provides greater adhesion to the underlying barrier layer than a copper layer plated at a lower plating potential in an acid bath. For copper to adhere to the barrier material, it is thought that copper ions must impinge on the barrier surface with sufficient energy to penetrate a thin oxidized or contaminated layer at the barrier surface. It is therefore believed that a copper layer deposited at a higher magnitude plating potential adhere is better to the exposed barrier layer during the plating process when compared to a layer plated using a smaller magnitude plating potential. This factor, combined with the inter-copper chemical bond between the PVD copper and the electrochemically deposited copper provides for an enhanced seed layer having excellent electrical as well as barrier adhesion properties. Such characteristics are also desirable for films used in blanket plating, full-fill plating, pattern plating, etc.

It has been found that the resistivity of the deposited copper film is directly related to the resistivity of the plating bath solution. Additives that assist in lowering the resistivity of the solution therefore provide a corresponding reduction in the resistivity of the deposited film.

Experimental results indicate that addition of ammonium sulfate significantly reduces the resistivity of the plating bath solution and, as such, the deposited film. The sheet resistance obtained for different amounts of ammonium sulfate are compared in the graph FIG. 4C. As can be seen, the highest sheet resistance, either with or without annealing at high temperatures, was obtained in the bath containing no ammonium sulfate. If ammonium hydroxide was used to adjust pH in which a trace amount of ammonium sulfate is introduced to the bath, the sheet resistance was reduced from 76 to 23. As the concentration of ammonium sulfate increased from 0.1 M to 0.5 M, the sheet resistance continuously decreased in a corresponding manner.

Although ammonium sulfate assists in reducing the sheet resistance of the deposited copper layer, experimental results indicate that it reduces the conformability of the resulting copper film. However, the addition of ethylene glycol to the ammonium sulfate containing solution substantially increases the conformability of the resulting deposit. FIG. 4D illustrates the relationship between the concentration of ethylene glycol and the conductivity of a plating solution containing 0.2M the of ammonium sulfate.

A preferred composition and range of concentrations for the various components of a plating bath having ammonium sulfate include the following:

1. Copper sulfate: 0.03M to 0.5M (preferably, 0.25M);
2. Complexing agent: complex to metal ratios from 1 to 4, preferably 2 using ED;
3. Ammonium sulfate: 0.01M to 0.5M, preferably 0.3M; and
4. Boric acid: 0.00 to 0.5M, preferably 0.2M.

As noted above, such a bath composition can be used for blanket plating, pattern plating, full-fill plating, and seed layer enhancement.

With reference again to the specific seed layer enhanced aspects of the present invention, the enhanced seed layer of FIG. 2C is suitable for subsequent electrochemical copper deposition. This subsequent copper deposition may take place in an alkaline bath within the apparatus employed to enhance the seed layer. This may be followed by a low-temperature annealing process that assists in lowering the resistivity of the deposited copper. Such a low-temperature annealing process preferably takes place at a temperature below about the 250 degrees Celsius and, more preferably, below about 100 degrees Celsius. When a low-K dielectric material is employed to isolate the copper structures, the upper annealing temperature limit should be chosen to be below the degradation temperature of the dielectric material.

Although the foregoing alkaline bath compositions may be used for the entire electrochemical deposition process, subsequent copper deposition may take place in an acid environment where plating rates are substantially higher than corresponding rates associated with alkaline plating baths. To this end, the semiconductor workpiece is preferably transferred to an apparatus wherein the workpiece is thoroughly rinsed with deionized water and then transferred to an apparatus similar to that of FIG. 3 wherein the plating bath is acidic. For example, one suitable copper bath comprises 170 g/l H_2SO_4 , 17 g/l copper and 70 ppm Chloride ions with organic additives. The organic additives are not absolutely necessary to the plating reaction. Rather, the organic additives may be used to produce desired film characteristics and provide better filling of the recessed structures on the wafer surface. The organic additives may include levelers, brighteners, wetting agents and ductility enhancers. It is during this deposition process that the trench 5 is substantially filled with a further layer of electrochemically deposited copper 22. The resulting filled cross-section is illustrated in FIG. 2D. After being filled in this manner, the barrier layer and the copper layers disposed above the trench are removed using any suitable process thereby leaving only the trench 5 with the copper metallization and associated barrier material as shown in FIG. 2E.

Use of an alkaline electrolytic bath to enhance the copper seed layer has particular advantages over utilizing acid copper baths without seed layer enhancement. After deposition of the PVD copper seed layer, the copper seed layer is typically exposed to an oxygen-containing environment. Oxygen readily converts metallic copper to copper oxide. If an acid copper bath is used to plate copper onto the seed layer after exposure of the seed layer to an oxygen containing environment, the acid copper bath would dissolve copper oxide that had formed, resulting in voids in the seed layer and poor uniformity of the copper layer deposited on the seed layer. Use of an alkaline copper bath in accordance with the disclosed embodiment avoids the problem by advantageously reducing any copper oxide at the surface of the seed layer to metallic copper. Another advantage of the alkaline copper bath is that the plated copper has much better adhesion to the barrier layer than that plated from an acid copper bath. Additional advantages of the seed layer enhancement aspects of the present invention can be seen from the following Example.

EXAMPLE 1

Comparison of Acid Copper Plating With and Without Seed Layer Enhancement

Semiconductor wafers 1, 2 and 3 were each coated with a 200 Angstrom PVD copper seed layer. In accordance with the present invention, wafers 1 and 2 had seed layer enhancement from citric acid and EDTA baths, respectively, the compositions of which are set forth below:

Bath for Wafer 1: 0.1 M $Cu SO_4$ +0.2 M Citric acid+0.05 M H_3BO_3 in D.I. water at pH 9.5, temperature 25° C.

Bath for Wafer 2: 0.1 M $Cu SO_4$ +0.2 M EDTA acid+0.05 H_3BO_3 in D.I. water at pH 12.5, temperature 25° C.

Wafer 3 did not have any seed layer enhancement.

The three wafers were then plated with a 1.5 micron copper layer from an acid copper bath under identical conditions. The following Table compares the uniformities, as deduced from sheet resistance measurements, of the three wafers after the deposition of a copper layer having a nominal thickness of 1.5 microns.

TABLE 1

Wafer	Enhancement Bath	Current Density	Non-uniformity Standard deviation (% , 1 σ)
1	Citrate	3 min. at 2 mA/cm ²	7.321
2	EDTA	3 min. at 2 mA/cm ²	6.233
3	None	0	46.10

As can be seen from the results in Table 1 above, seed layer enhancement in accordance with the disclosed process provides excellent uniformity (6 to 7%) compared to that without seed layer enhancement (46%). This is consistent with observations during visual examination of the wafer after 1.5 micron electroplated copper had been deposited. Such visual examination of the wafer revealed the presence of defects at wafer electrode contact points on the wafer without seed layer enhancement.

FIGS. 5, 6A and 6B are photographs taken using a SEM. In FIG. 5, an ultra-thin seed layer has been deposited on the surface of a semiconductor wafer, including micro-structures, such as trenches 85. As shown, void regions are present at the lower corners of the trenches. In FIG. 6A, the seed layer has been enhanced in the manner described above in a bath containing citric acid as the complexing agent. This enhancement resulted in a conformal copper seed layer that is very suited for subsequent electrochemical deposition of copper metallization.

FIG. 6B illustrates a seed layer that has been enhanced in a bath containing EDTA as the complexing agent. The resulting seed layer includes larger grain sizes that project as spikes from the sidewalls of the trenches. These sidewall grain projections make subsequent electrochemical deposition filling of the trenches more difficult since they localize a higher plating rate resulting in non-uniformity of the subsequent electrochemical deposition. This effect is particularly noticeable in recessed micro-structures having small dimensions. As such, a complexing agent such as citric acid is more preferable when filling small micro-structures. Results comparable for copper baths containing citric acid have also been achieved using ED as the complexing agent.

FIG. 7 is a schematic representation of a section of a semiconductor manufacturing line 90 suitable for implementing the foregoing processes. The line 90 includes a

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vapor deposition tool or tool set 95 and an electrochemical copper deposition tool or tool set 100. Transfer of wafers between the tools/tool sets 95 and 100 may be implemented manually or through an automated transfer mechanism 105. Preferably, automated transfer mechanism 105 transfers workpieces in a pod or similar environment. Alternatively, the transfer mechanism 105 may transfer wafers individually or in an open carrier through a clean atmosphere joining the tools/tool sets.

In operation, vapor deposition tool/tool set 95 is utilized to apply an ultra-thin copper seed layer over at least portions of semiconductor workpieces that are processed on line 90. Preferably, this is done using a PVD application process. Workpieces with the ultra-thin seed layer are then transferred to tool/tool set 100, either individually or in batches, where they are subject to electrochemical seed layer enhancement at, for example, processing station 10. Processing station 10 may be constructed in the manner set forth in FIG. 3. After enhancement is completed, the workpieces are subject to a full electrochemical deposition process in which copper metallization is applied to the workpiece to a desired interconnect metallization thickness. This latter process may take place at station 110, but preferably occurs at further processing station 115 which deposits the copper metallization in the presence of an acidic plating bath. Before transfer to station 115, the workpiece is preferably rinsed in DI water at station 112. Transfer of the wafers between stations 110, 112, and 115 may be automated by a wafer conveying system 120. The electrochemical deposition tool set 100 may be implemented using, for example, an LT-210™ model or an Equinox™ model plating tool available from Semitool, Inc., of Kalispell, MT.

Numerous modifications may be made to the foregoing system without departing from the basic teachings thereof. Although the present invention has been described in substantial detail with reference to one or more specific embodiments, those of skill in the art will recognize that changes may be made thereto without departing from the scope and spirit of the invention as set forth in the appended claims.

What is claimed is:

1. A process for applying a metal structure to a workpiece comprising:

providing a first electroplating bath including copper sulfate as a source of metal ions as a principal metal species to be deposited during subsequent electroplating, ammonium sulfate, a complexing agent, and ethylene glycol;

providing a workpiece on which one or more microelectronic devices are to be formed;

exposing at least one surface of the workpiece to the first electroplating bath;

providing electroplating power between the at least one surface of the workpiece and an anode disposed in electrical contact with the first electroplating bath to electroplate copper onto the at least one surface of the workpiece in an electrolytic first deposition process; and

depositing additional copper onto the copper deposited in the first deposition process using a second deposition process that is different than the first electrolytic deposition process.

2. The process of claim 1, wherein the copper sulfate is included at a level of 0.03 to 0.25 M.

3. The process of claim 1, wherein the first electroplating bath comprises an alkaline bath.

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4. The process of claim 3, wherein the alkaline bath has a pH of at least 9.0.

5. The process of claim 3, wherein the alkaline bath is pH adjusted with an alkaline agent selected from the group consisting of potassium hydroxide, ammonium hydroxide, tetramethylammonium hydroxide and sodium hydroxide.

6. The process of claim 1, wherein the second deposition process occurs in an acidic electrolytic bath.

7. The process of claim 1, wherein metal is deposited in the second deposition process at a higher rate than in the first deposition process.

8. The process of claim 1, wherein the ammonium sulfate is included at a level of 0.1 to 0.5 M.

9. The process of claim 1, further comprising depositing a barrier layer on the surface of the workpiece before the first deposition process.

10. The process of claim 9, wherein metal is plated directly onto the barrier layer in the first deposition process.

11. The process of claim 9, further comprising depositing an ultra-thin seed layer of metal onto the barrier layer before the first deposition process.

12. The process of claim 1, wherein the complexing agent is selected from the group consisting of ED, EDTA, and a polycarboxylic acid.

13. The process of claim 12, wherein the complexing agent is citric acid.

14. A process for applying a metal structure to a workpiece comprising:

providing a first electroplating bath including copper sulfate as a source of metal ions as a principal metal species to be deposited during subsequent electroplating, a complexing agent, and ethylene glycol;

providing a workpiece on which one or more microelectronic devices are to be formed,

exposing at least one surface of the workpiece to the first electroplating bath;

providing electroplating power between the at least one surface of the workpiece and an anode disposed in electrical contact with the first electroplating bath to electroplate copper onto the at least one surface of the workpiece in an electrolytic first deposition process at a first deposition rate; and

depositing additional copper onto the copper deposited in the first deposition process using a second deposition process at a second deposition rate that is higher than the first deposition rate.

15. A process for applying a metal structure to a workpiece comprising:

providing a workpiece on which one or more microelectronic devices are to be formed;

depositing a barrier layer on at least one surface of a workpiece;

providing a first electroplating bath including copper sulfate as a source of principal metal species to be deposited during subsequent electroplating, ethylene glycol, a metal ion complexing agent, and an alkaline agent in an amount to adjust the pH of the first electroplating bath to a pH of at least 9.0;

exposing the least one surface of the workpiece including the barrier layer to the first electroplating bath;

providing electroplating power between the at least one surface of the workpiece and an anode disposed in electrical contact with the first electroplating bath to electroplate copper directly onto the barrier layer of the workpiece in an electrolytic first deposition process; and

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depositing additional copper onto the copper deposited in the first deposition process using a second deposition process at a second deposition rate that is higher than a rate at which copper is deposited in the first deposition process.

16. The process of claim 15, wherein the alkaline agent selected from the group consisting of potassium hydroxide, ammonium hydroxide, tetramethylammonium hydroxide and sodium hydroxide.

17. The process of claim 15, wherein the second deposition process occurs in an acidic electrolytic bath.

18. The process of claim 15, wherein the complexing agent is selected from the group consisting of ED, EDTA, and a polycarboxylic acid.

19. The process of claim 18, wherein the complexing agent is citric acid.

20. A process for applying a metal structure to a workpiece comprising:

providing a first electroplating bath including copper sulfate as a source of metal ions as a principal metal species to be deposited during subsequent electroplating, a complexing agent, ethylene glycol, and an alkaline agent in an amount sufficient to raise the pH of the bath to at least 9.0;

providing a workpiece on which one or more microelectronic devices are to be formed;

exposing at least one surface of the workpiece to the first electroplating bath;

providing electroplating power between the at least one surface of the workpiece and an anode disposed in

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electrical contact with the first electroplating bath to electroplate copper onto the at least one surface of the workpiece in an electrolytic first deposition process; and

5 depositing additional copper onto the copper deposited in the first deposition process using a second deposition process that is different than the first electrolytic deposition process.

21. A copper electroplating solution comprising copper sulfate as a source of copper ions at a level so as to be the principal metal species, ammonium sulfate, and ethylene glycol at a level of greater than 0 to 1.0 Molar, the solution being formulated so as to be suitable for electrodeposition of copper onto a microelectronic workpiece.

22. The solution of claim 21, further comprising a complexing agent.

23. The solution of claim 22 wherein the complexing agent is selected from the group consisting of ED, EDTA, and a polycarboxylic acid.

24. The solution of claim 23 wherein the complexing agent is citric acid.

25. The solution of claim 21, further comprising an alkaline agent in an amount sufficient to increase the pH of the solution to at least 9.0.

26. The solution of claim 21, wherein the ammonium sulfate is included at the level of 0.1 to 0.5 M.

27. The solution of claim 21, further comprising boric acid at a level of 0.01 Molar to 0.5 Molar.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,290,833 B1
DATED : September 18, 2001
INVENTOR(S) : Linlin Chen

Page 1 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,

Item [54], **ABSTRACT,**

Line 12, "provide" should be -- provides --

Column 1,

Lines 8-15, "This is a continuation ... filed May 15, 1998." should be -- This is a continuation application of International PCT Patent Application No. PCT/US99/06306, designating the US, filed March 22, 1999, entitled APPARATUS AND METHOD FOR ELECTROLYTICALLY DEPOSITING COPPER ON A SEMICONDUCTOR WORKPIECE, which claims priority from US Patent Application Serial No. 09/045,245, filed March 20, 1998, now US Patent No. 6,197,181, and US Patent Application Serial No. 60/085,675, filed May 15, 1998. --

Line 36, "Single Metallization Level" should be -- Single Metallization Level --

Line 40, "Substrate" should be -- Substrate --

Line 44, "Workpiece" should be -- Workpiece --

Column 2,

Line 12, " $\tau = RC[1 + (V_{SAT}/RI_{SAT})]$ " should be -- $\tau = RC[1 + (V_{SAT}/RI_{SAT})]$ --

Line 14, " I_{SAT} " should be -- I_{SAT} --.

Line 15, " V_{SAT} " should be -- V_{SAT} --

Lines 21, 25 and 28, " Ke " should be -- Ke --

Line 23, " V_{SAT}/RI_{SAT} " should be -- V_{SAT}/RI_{SAT} --

Lines 33 and 34, " $\mu\Omega\text{cm}$ " should be -- $\mu\Omega\text{cm}$ --

Column 3,

Line 4, "result" should be -- results --

Line 40, "provide" should be -- provides --

Column 4,

Lines 52, 54 and 57, "eletromicrograph" should be -- electromicrograph --

Column 5,

Line 21, "to to" should be -- to --

Column 6,

Line 34, "1600" should be -- to 1600 --

Line 47, "micro-structures" should be -- micro-structures. --

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,290,833 B1
DATED : September 18, 2001
INVENTOR(S) : Linlin Chen

Page 2 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 7,

Line 28, "pII" should be -- pH --

Line 38, "with 25° C." should be -- with 25° C --

Column 8,

Lines 58 and 61, "conformability" should be -- conformality --

Line 64, "the of" should be -- of --

Column 9,

Line 19, "the 250" should be -- 250 --

Column 10,

Line 46, "comers" should be -- corners --

Column 11,

Lines 17 and 18, "10" should be -- 110 --

Column 12,

Line 3, "3" should be -- 4 --

Column 13,

Line 24, "pII" should be -- pH --

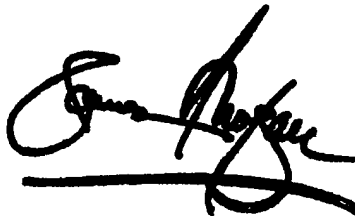
Column 14,

Line 13, "levl" should be -- level --

Signed and Sealed this

Eighth Day of October, 2002

Attest:



Attesting Officer

JAMES E. ROGAN
Director of the United States Patent and Trademark Office